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# Effect of addition of salts on hydrogen overvoltage

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# NOTE TO USERS

# EFFECT OF ADDITION OF SALTS ON HYDROGEN OVERVOLTAGE

by

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## STATEMENT OF PROBLEM

The purpose of the investigation was to determine what effect, if any, the addition of "indifferent" salts to an electrolyte has upon hydrogen overvoltage.

In connection with this work "indifferent" salts were considered to be those salts that, when added to the electrolyte of the cell, would not materially alter the reversible potential of the cell either by hydrolyzing, acting as a depolarizing agent, or depositing metal (instead of hydrogen) on the cathode. Thus was eliminated from consideration any salt that ordinarily would be expected to furnish a chemical individual that is capable of reacting chemically at the cathode surface. A limitation of this kind was necessary so that these extraneous effects would not be mistaken for a change in hydrogen overvoltage.

Further, by hydrogen overvoltage was meant the difference between the potential developed on the test electrode under the existing conditions and the potential of a reversible hydrogen electrode in the same solution. This means that the density of the polarizing current must have been, and was, specified for each measured value of overvoltage.

The suggestions for this investigation arose from a consideration of two widely known and well recognized phenomena, namely: (1) the effect that the presence of indifferent

salts has on the corrosion rate of metals; and (2) the close relationship that exists between overvoltage and corrosion rate. Because the existence of these two phenomena is well established, it was thought that a relationship might exist between overvoltage and the presence of indifferent salts in the cell electrolyte.

The choice of iron for the test electrode was influenced by the knowledge that corrosion of iron is hindered in the presence of certain salts. An added reason for the choice of iron was that it belongs to the moderately "active" group of metals. Considerable work has been done on the effect of electrolyte composition on overvoltage using the inactive metals, mercury and lead; on the other hand, only a little work in this field has been done using an active metal. Moreover, iron may be used in contact with an alkaline solution as hydrogen electrode, but mercury and lead cannot.

The investigation had four objectives, namely: (1) to determine the effect of different cations, (2) to determine the effect of different anions, (3) to determine the effect of adding different salt concentrations to solutions having the same base concentration, and (4) to determine the effect of varying the base concentration in solutions having the same salt concentration.

# INTRODUCTION

In the field of science treating with metallic corrosion phenomena, the electrolytic theory is generally considered to afford a reasonable explanation for a large part of such phenomena. In brief, the theory states that local conditions of strain, variations in composition, crystal orientation, etc., cause galvanic cells to be formed whenever the metal is brought into contact with an electrolyte. That is, different portions of the metal act as positive and negative electrodes, respectively, and the liquid in contact with the metal serves as the cell electrode. Any one or several of the usual electrode processes may occur at these electrode areas. Usually, however, it is thought that metal dissolves from the anodic portions and hydrogen is evolved on the cathodic areas. The dissolution of the metal constitutes metallic corrosion.

Corrosion of metals may be hindered, therefore, by means of any process that increases the resistance in the local galvanic cells or, and this is more pertinent to this research, decreases the difference in the effective potential that exists between the cathodic and anodic portions of the metal. The effective potential is the difference between the reversible potentials of the positive and negative electrodes less the overvoltage and polarization effects. Both of these latter act as back electromotive forces. The current that

can flow through the cell is proportional to the effective potential; hence, the current (and the amount of corrosion) is decreased whenever the overvoltage is increased.

Therefore, it is desirable to consider: first, the various factors that are known to affect overvoltage; and, second, the theories that have been advanced in order to explain the experimental observations. There are, however, some qualifications to be made. The experimental and theoretical results arising from the use of the commutator method for measuring overvoltages will be given no great consideration. This is justifiable inasmuch as many investigators[9,12,13,17,26] have shown that results obtained by this method prior to 1925 have no real significance. In addition, any significant results obtained since 1925 have the same significance as those that are obtained from the employment of the direct method. Furthermore, since there is wide disagreement between the methods for determining minimum overvoltages and no real proof[1,2] that such a thing exists, no consideration will be given to minimum overvoltage. All this means, therefore, that the present discussion will be limited to results and relationships derived from the measurements of overvoltage by the direct method with measurable currents flowing.

# LITERATURE SURVEY

## Facts About Overvoltage

The principal factors which have been found to affect overvoltage are: kind of metal; condition of surface; previous treatment of electrode; time; current density; temperature; composition of the electrolyte.

Kind of metal.

Metals vary widely among themselves as to the ease of attainment of the reversible hydrogen potential. With certain metals, examples of which are Pd, Pt, Au, and Ni, the reversible hydrogen potential can be easily reached; whereas on others, such as Pb, Hg, and Cu, the reversible hydrogen potential has never been developed. Hereafter, the first-named group will be designated the "electrochemically active" metals; the last-named group will be called "electrochemically inactive." On some electrochemically active metals considerable current can be made to flow before an appreciable increase of the potential from the reversible can be observed. On the other hand, Hg has a considerable overvoltage even at extremely minute current densities.

Condition of surface.

The activity depends not only on the type of metal but also on the condition of the surface and its previous treatment. Widely variant results are obtained, for instance, with Pt that has either a spongy, rough or smooth surface. Some of the variance may be accounted for if the "true" surface area is used in calculating the current density rather than the apparent or measured area. By true area is meant the total area of the exposed rough surface, which is sometimes hundreds of times larger than that calculated from the dimensions of the surface. The true area may be determined experimentally if one treats the Helmholtz double layer at the electrode surface as a plate condenser. Nevertheless, there yet exists a difference in overvoltage which may be attributed to different degrees of activity in the surface condition itself[28]. This is probably related to the catalytic activity of the surface.

Previous treatment.

The difference in activity brought about by different kinds of preliminary treatment is due, in all probability, to different kinds of surface thus produced. Some of the electrode treatments are as follows: manifold oxidation and reduction in atmospheres of oxygen and hydrogen, respectively; oxidation by anodic polarization; heating in vacuo followed

by heating in an atmosphere of hydrogen[31]; polishing with emery cloth; production of a fresh surface within the electrolyte[25,29]; and combinations of the above treatments.

Time.

The overvoltage may change profoundly with time. This temporal change in activity occurs with many metals even when the electrolyte has been carefully purified and freed from traces of oxygen; hence, though it may be considered a "poisoning" of the electrode by hydrogen itself, the decreased activity is more probably an effect of a change in the surface condition of the metal. A visible alteration in the electrode surface can be observed in many instances. The most active metals are more sensitive to deactivation processes than the less active; thus, on all the active metals, considerable increases in overvoltage with time take place, but no such increase occurs on a Hg cathode.

However, in the initial stage of the electrolysis, a different kind of temporal alteration in overvoltage takes place. This temporal change is very rapid, and with an appreciable constant current density the change of overvoltage is linear with time[3]. With any kind of smooth surface a constant quantity of electricity (namely, $6 \times 10^{-7}$ coulombs per square centimeter) is found to effect a change of 100 millivolts in overvoltage. The same quantity is required whether polarization or depolarization of the electrode is

taking place. This quantity of electricity is only enough to form about 1/3000 of a single layer of hydrogen atoms[4]. The quantity of electricity necessary to change from a reversible oxygen electrode to a reversible hydrogen electrode is $9 \times 10^{-4}$ coulombs, enough to replace with hydrogen the oxygen absorbed on each accessible metal atom but not enough to form a continuous layer of mutually touching hydrogen atoms.

Current density.

Tafel found in 1905[34] that an empirical equation could be written relating the overvoltage $\eta$ to the current density i , namely,

$$\eta = a + b \log i$$

In this equation a is a constant characteristic of a metal in a given physical state, and b is a nearly universal constant at a given temperature. In most instances b has a value of 0.12 at room temperature; however, the value of b may decrease to nearly one-fourth of this in the case of very active metals.

Theoretical reasons led Tafel to believe that b should be a function of the absolute temperature according to the following equation,

$$b = 2.3\ RT/\alpha F.$$

Theoretically, $\alpha$ should have been equal to 2, but experimentally it turned out to be very close to 0.5. That is, at

20°C and $\alpha = 2$, b is calculated to be 0.029; but with $\alpha = 0.5$, b has the experimentally determined value 0.116. Very little work has been done to confirm the relationship between b and T; however, Bowden[4] has found the equation to be valid over the limited range of temperatures at which he worked and for the few electrode materials that he studied.

Composition of the electrolyte.

Within the last two decades much of the experimental work has been concerned with the composition of the electrolyte. This work may be roughly classified into three general groups: (1) effect of organic inhibitors and poisons; (2) effect of hydrogen-ion concentration; and (3) effect of presence of neutral, or indifferent, salts in the electrolyte. Only the latter two effects need be discussed here since the first effect is not pertinent to the research. Moreover, the effects of hydrogen-ion concentration and of presence of indifferent salts have often been studied concurrently. Such was the case when Glasstone investigated these effects.

He employed mercury and lead[13] cathodes, acid and alkaline electrolytes, and potassium sulfate as an added indifferent electrolyte. His results show a small shift in overvoltage in all cases. This shift appeared negligible to him, however, in view of the large changes in hydrogen-ion concentration to which they corresponded. A typical table is presented below:

Table 1

Hydrogen Overvoltage in Sulfuric Acid Solutions with Lead Cathodes

| Electrolyte | Current Density in amp/cm$^2$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | min. | 0.002 | 0.004 | 0.008 | 0.0016 | 0.032 | 0.12 |
| 8N-$H_2SO_4$ | 0.62 | 0.74 | 0.77 | 0.80 | 0.82 | | |
| N-$H_2SO_4$ | 0.62 | 0.76 | 0.79 | 0.81 | 0.84 | | |
| N/16-$H_2SO_4$ | 0.62 | 0.77 | 0.81 | 0.83 | 0.86 | | |
| N/16-$H_2SO_4$ + N/16-$K_2SO_4$ | 0.62 | 0.82 | 0.88 | 0.95 | 1.05 | 1.27 | 1.37 |
| N/16-$H_2SO_4$ + N/4-$K_2SO_4$ | 0.62 | 0.85 | 0.90 | 0.95 | 1.21 | 1.27 | 1.36 |
| N/16-$H_2SO_4$ + N-$K_2SO_4$ | 0.62 | 0.89 | 0.97 | 1.09 | 1.19 | 1.24 | 1.36 |

Glasstone interprets the results in this manner: (1) a thirtyfold change in hydrogen-ion concentration causes a change of only a few hundredths of a volt; therefore, overvoltage is constant with changing acid concentration; (2) the effect of the added alkali ions increases with increasing current density; hence, there probably exists a codeposition of hydrogen and alkali metal forming an alloy with lead. Herasymenko[20] has adapted a contrary opinion. He points out that the variation in overvoltage is of the same order of magnitude as the variation in the Nernst potential. Furthermore, he shows with some of his own results that the hydrogen-ion concentration in sulfuric acid-potassium sulfate solutions is considerably affected by the concentration of the potassium sulfate. He demonstrates that his own results, as well as Glasstone's, conform to an equation deduced by Heyrovský. This equation relates overvoltage to the concentration of hydrogen ions as well as to the current density

as follows:

$$\eta = \frac{RT}{F} \ln i + \frac{RT}{F} \ln(H^+) + \text{constant.}$$

However, both Glasstone and Herasymenko relied heavily on the data corresponding to minimum overvoltage. Hence the importance of their data and results should be minimized. In particular, Glasstone's conclusions were based largely on overvoltage data for which no current densities were specified. Indeed, these latter may have varied considerably in the respective measurements of minimum overvoltages; therefore, his basis of comparison was seriously at fault. Herasymenko, on the other hand, plotted the current density, i, against potential of cathode, $\pi$, and used values of $\pi$ corresponding to the same slopes $di/d\pi$ for his comparisons. Since the relationship between i and $\pi$ is logarithmic the exact value of $\pi$ at any $di/d\pi$ depends on the scale on which the curve is drawn. The value of $\pi$ at one arbitrary value of $di/d\pi$ was designated the "hydrogen deposition potential"; these values were used in comparisons.

In spite of the weaknesses evident in the works of Glasstone and Herasymenko, Bowden[2] was able, happily, to confirm the conflicting conclusions of both investigators. Employing special precautions as to purity of mercury electrode, purity of electrolyte, and freedom from traces of oxygen and poisons, he was able to obtain data for current densities as low as $10^{-8}$ amp/cm$^2$. He first used a quiet pool of mercury

as the cathode and employed current densities ranging from $10^{-8}$ to $10^{-2}$ amp/cm$^2$; the results for the higher current densities were later checked by means of the dropping mercury electrode. By plotting the overvoltage against the logarithm of the current density he found that two straight lines were obtained--Curve I for the lower densities, Curve II for the higher densities--with slopes of 0.12 and 0.22 respectively. One Curve I could be used to show graphically the data obtained at the low densities for six solutions of pH values ranging from 0.8 to 6.6 with an accuracy of ±30 millivolts; at the higher densities, however, the corresponding points on Curves II differed by 58 millivolts for each pH unit. These latter lines had the same slope, 0.22, and approximately the same starting point; that is, the break in the data, corresponding to a transition from Curve I to Curve II, always occurred at approximately one milliamp per square centimeter. However, data were obtained fitting Curve II for lower current densities by starting with high current densities and decreasing the current; when this was done the potential was subject to sudden drop to Curve I. Inasmuch as his data were obtained using solutions of different compositions, Bowden could deduce that overvoltages corresponding to Curves I were independent of the composition of the electrolyte; on the other hand, overvoltages corresponding to Curves II have the same dependence on pH as do Nernst potentials but are otherwise independent of the composition of the electrolyte.

Bowden notes that Glasstone's minimum overvoltages lay in the region of his Curve I, and thus explains the latter's conclusion that overvoltages are independent of the pH. On the other hand, Herasymenko's hydrogen deposition potentials fall in the region of Curve II, and this, therefore, confirms his deduction that overvoltage is dependent on pH. Incidentally, Bowden observed that the existence of the state conforming to Curves II was more easily produced and maintained in the more dilute solutions.

Later Herasymenko and Šlendyk[21] were able to confirm the former's original work and to enlarge upon it. In this work they still use the term hydrogen deposition potentials, but now they define this quantity as the potential corresponding to a definite, but unspecified by them, current density. They found that in hydrochloric acid solutions an increase in overvoltage occurred as the solutions were diluted. This increase per tenfold dilution became greater the less the concentration: thus the difference in overvoltage between solutions having pH values one and two was 5 millivolts; whereas, the difference in solutions of pH three and four was 42 millivolts. Hence, it appears that the effect of hydrogen-ion concentration on overvoltage approaches the effect on Nernst potential (58 millivolts) in the lower hydrogen-ion concentrations.

These investigators extended their work to include the

effect of neutral-salt additions on overvoltage. In this connection they used the chlorides of the alkali metals, the alkaline earth metals, magnesium, lanthanum, and thorium. Various concentrations of these salts were superimposed on various concentrations of hydrochloric acid as demonstrated in the following tables. The normal calomel electrode was used in all cases as a reference electrode.

In Tables 2 and 6, $\Delta\pi$ and $\Delta\eta$ refer to the difference between the $\pi$'s and $\eta$'s, respectively, of the successive normalities. In Tables 3, 4, and 5, $\Delta\pi$ refers to the difference between the $\pi$ of the solution indicated and the $\pi$ of the pure acid solution.

Table 2

Pure Hydrochloric Acid Solutions in Water

| Normality | Separation potential $\pi$ (in volts) | Difference $\Delta\pi$ (in volts) | Difference in overvoltages $\Delta\eta$ (in volts) |
|---|---|---|---|
| $10^{-1}$ | 1.224 | | |
| $10^{-2}$ | 1.286 | 0.062 | 0.005 |
| $10^{-3}$ | 1.378 | 0.092 | 0.036 |
| $10^{-4}$ | 1.476 | 0.098 | 0.041 |

Table 3

Salts Added to 0.1N-HCl Solutions

| Normality of Added Salt | KCl | | $BaCl_2$ | |
|---|---|---|---|---|
| | $\pi$ | $\Delta\pi$ | $\pi$ | $\Delta\pi$ |
| 0 | 1.224 volt | | | |
| $10^{-4}$ | | | 1.236 | 0.012 |
| $10^{-3}$ | 1.235 | 0.011 | 1.250 | 0.026 |
| $10^{-2}$ | 1.241 | 0.017 | 1.276 | 0.056 |
| $10^{-1}$ | 1.265 | 0.031 | 1.285 | 0.061 |
| 1 | | | 1.287 | 0.063 |

Table 4

Salts Added to 0.01N-HCl Solutions

| Normality of Added Salts | LiCl | NaCl | KCl | RbCl | $MgCl_2$ | $CaCl_2$ $SrCl_2$ $BaCl_2$ |
|---|---|---|---|---|---|---|
| | $\pi$ | $\pi$ | $\pi$ | $\pi$ | $\pi$ | $\pi$ |
| 0 | 1.286 volt | | | | | |
| $10^{-4}$ | | | | | 1.313 | 1.316 |
| $10^{-3}$ | 1.299 | 1.306 | 1.306 | 1.308 | 1.340 | 1.343 |
| $10^{-2}$ | 1.308 | 1.321 | 1.326 | 1.329 | 1.364 | 1.368 |
| $10^{-1}$ | 1.339 | 1.350 | 1.360 | 1.372 | 1.387 | 1.393 |
| 1 | | | | | | 1.395 |

Table 5

Salts Added to 0.01N-HCl Solution

| Normality of Added Salt | $LaCl_3$ | | $ThCl_4$ | |
|---|---|---|---|---|
| | $\pi$ | $\Delta\pi$ | $\pi$ | $\Delta\pi$ |
| 0 | 1.286 volt | | | |
| $10^{-6}$ | 1.307 | 0.021 | 1.307 | 0.021 |
| $10^{-5}$ | 1.315 | 0.029 | 1.331 | 0.045 |
| $10^{-4}$ | 1.339 | 0.053 | 1.355 | 0.069 |
| $10^{-3}$ | 1.365 | 0.079 | 1.390 | 0.104 |

Table 6

Solution of 1N-$BaCl_2$ in Varying Concentrations of HCl

| Normality of HCl | Separation potential $\pi$ (in volts) | Difference $\Delta\pi$ (in volts) |
|---|---|---|
| $10^{-1}$ | 1.287 | |
| $10^{-2}$ | 1.393 | 0.106 |
| $10^{-3}$ | 1.509 | 0.116 |
| $10^{-4}$ | 1.630 | 0.121 |

It will be noted that the displacement of the separation potential* is influenced to a large extent by the valence of

*It is to be regretted that the investigators did not determine the reversible hydrogen potential in the various salt solutions. That it does not differ appreciably from that in the pure acid solutions is probable; therefore, the displacement of the separation potential is equivalent to the displacement of the overvoltage (i.e., $\pi - \pi_R = \eta$ and $\pi_R$=const. at constant $C_{H^+}$).

the ion. Thus the concentration of ions required to yield a given displacement forms the following series:

$$(Th^{++++}) < (La^{+++}) < (Ba^{++}) < (K^{+}).$$

The flocculation of negative colloids by means of positively charged ions follows the same series. A more remarkable feature is that the concentrations of ions of the same valence yield a series similar to that found in numerous other electrokinetic phenomena, namely:

$$(Rb^{+}) < (K^{+}) < (Na^{+}) < (Li^{+}).$$

These facts lead naturally to the conclusions that the ions are adsorbed in the double layer and this adsorption is dependent exponentially on the charge of the ion as well as on other specific properties of the ion.

Other significant facts to be remembered from these data are: (1) the more concentrated the acid solution is, the greater the concentration the added salt must have in order to produce the same displacement of overvoltage; (2) as the concentration of added salt increases, the displacement of the separation potential from that in pure acid solutions approaches a maximum limiting value; (3) the difference in the limiting values of two solutions differing in pH by one unit closely approximates 2RT/F; (4) it is evident, therefore, that the effect on overvoltage is equivalent to the effect on Nernst potential.

The same conclusions may be drawn from later work which was performed by Levina and Zarinskiĭ[29,30]. They employed carefully prepared and purified material and provided for the quick and easy renewal of the mercury surface. The first work was done on pure acid solutions from which they obtained results which agreed with measurements of Bowden at low current densities but disagreed at the higher current densities. That is, these investigators found that the overvoltage-current density curves obeyed Tafels equation with b = 0.12 for the entire course of the curve from $10^{-8}$ to $10^{-3}$ amp/cm$^2$.

These same authors then investigated the effect of adding $LaCl_3$ to the solution and obtained results qualitatively the same as those of Herasymenko and Šlendyk. The following table summarizes their results:

Table 7

Magnitude of Overvoltage in Presence of Excess of $LaCl_3$
(Current density = $2.45 \cdot 10^{-6}$ amp/cm$^2$)

| HCl Concentration | $\eta$ (in volts) | $\Delta\eta$ (in volts) |
|---|---|---|
| $10^{-3}$N | 0.890 | |
| $10^{-2}$N | 0.836 | 0.054 |
| $10^{-1}$N | 0.790 | 0.046 |

An interesting investigation[31] by Lukovtsev, Levina, and Frumkin using nickel as the test electrode gave somewhat different results. These investigators worked with both acid

and alkaline solutions. Extraordinary care was observed to prepare pure solutions of hydrochloric acid and sodium hydroxide and to prevent contamination. Similar care was observed in the preparation of the $LaCl_3$-HCl solutions and the NaCl-NaOH solutions. Their data were not presented in the form of tables but a clear picture of their results may be obtained by reference to Figures 1, 2, 3, and 4.

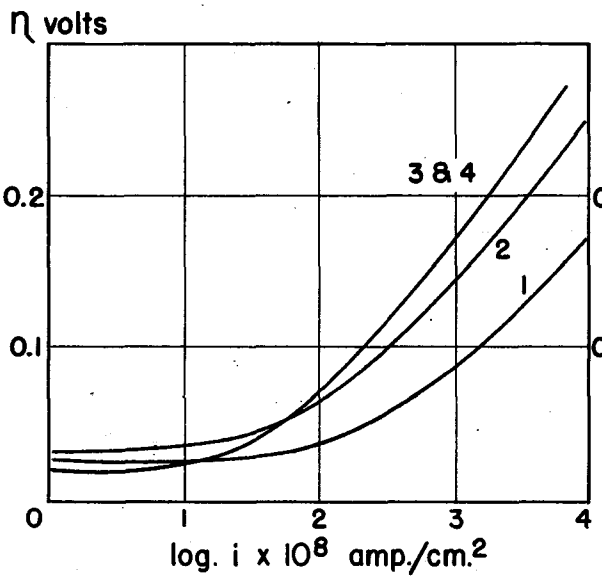


Fig. 1. Dependence of H-overvoltage on current density in acid solutions
(1) 0.15N-HCl;
(2) 0.013N-HCl;
(3) 0.0012N-HCl;
(4) 0.0003N-HCl.

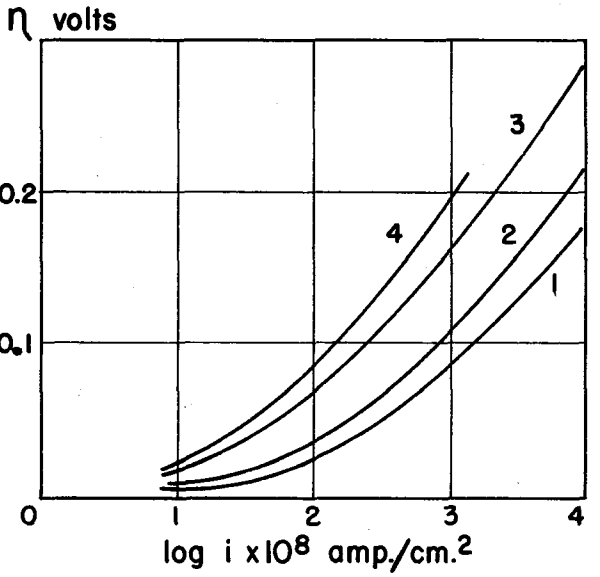


Fig. 2. Dependence of H-overvoltage on current density in alkaline solutions
(1) 0.42N-NaOH;
(2) 0.047N-NaOH;
(3) 0.0075N-NaOH;
(4) 0.001N-NaOH.

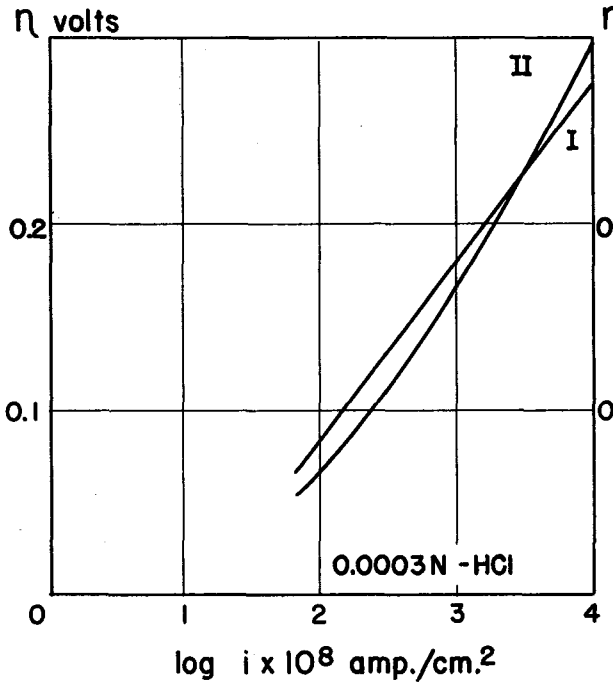


Fig. 3. Effect of $LaCl_3$ on overvoltage in acid solutions
Curve I - Pure HCl
Curve II - Same plus 0.001N-$LaCl_3$

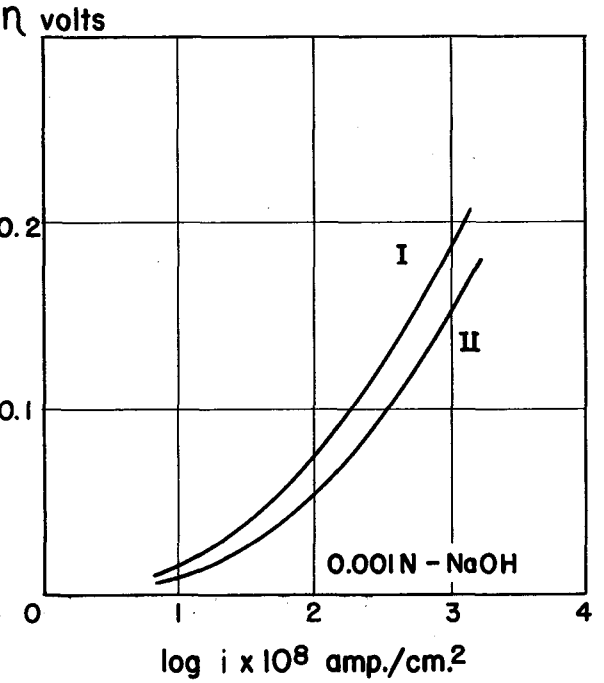


Fig. 4. Effect of NaCl on overvoltage in alkalies
Curve I - Pure NaOH
Curve II - Same plus 0.1N-NaCl

From Figure 1 it becomes apparent that the laws governing the behavior of hydrogen overvoltage on nickel electrodes deviate from those on mercury electrodes. That is, overvoltage in pure acid solutions is dependent on the $H^+$-ion concentration. This dependence holds only in the more concentrated solutions; furthermore, a study of Figure 2 shows that overvoltage is a function of $H^+$-ion concentration in the more concentrated solutions of alkali but approaches a constant value for the more dilute solution. Thus, the interesting observation is made that overvoltage increases (by about 58 mv per tenfold dilution) with dilution in both acid and

alkaline solutions.

The effect of the addition of $LaCl_3$ on overvoltage in HCl solutions is somewhat anomalous. At low current densities (below $3 \times 10^{-5}$ amp/cm) the addition of this salt decreases the overvoltage but in the higher current densities the overvoltage is increased. The explanation the investigators gave for this phenomenon is that nickel apparently has a positive charge with respect to the solution at the lower current densities; on increasing the polarization the charge passes through a zero at the point where addition of $LaCl_3$ has no effect on overvoltage.

The addition of NaCl to the more dilute solutions of alkali (0.001 and 0.0075N) causes a decrease in overvoltage which is less the greater the concentration of alkali.

Equations were deduced to fit the data for both acid and alkali solutions, namely:

for acid -

$$\eta - \zeta = 2RT/F \ln i - RT/F \ln C_{H^+} + \text{const.}$$

for alkali

$$\eta + \zeta = 2RT/F \ln i - RT/F \ln C_{OH^-} + \text{const.}$$

The effect of surface-active ions on overvoltage has been studied by Iofa, Kabanoff, Kuchinski, and Christyakov[23]. They used mercury as their test electrode and it was used according to both the quiet pool and the dropping method. Their solutions were carefully prepared. The essential part of

their results is shown graphically in Figures 5 and 6. Reference to Figure 5 shows that surface-active anions lower the overvoltage; on the other hand, Figure 6 shows that surface-active cations raise the overvoltage.

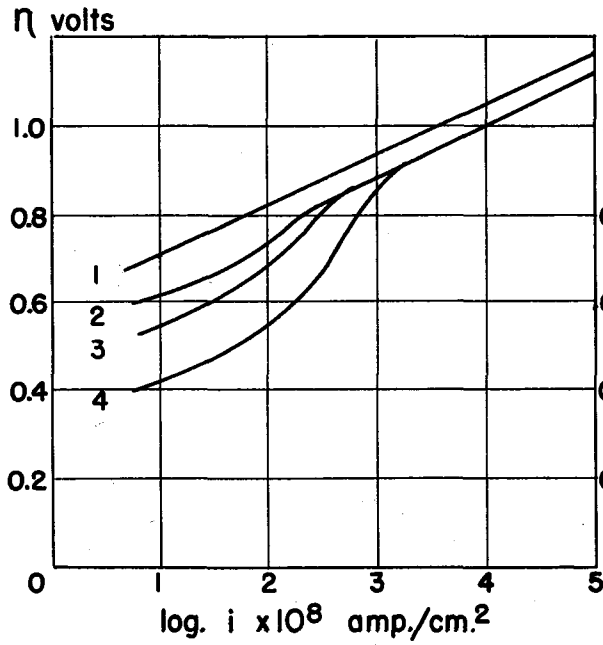


Fig. 5. $\eta$ - ln i curves
(1) 1N-$Na_2SO_4$ + 0.1N-$Na_2SO_4$
(2) 1N-KCl + 0.1N-HCl
(3) 1N-KBr + 0.1N-HCl
(4) 1N-KI + 0.1N-HCl

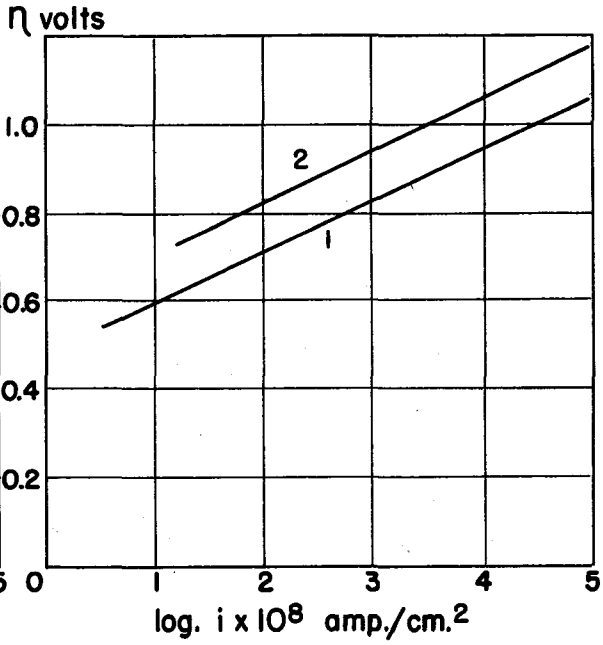


Fig. 6. $\eta$ - ln i curves
(1) 1N-$H_2SO_4$
(2) 1N-$H_2SO_4$ + 0.025N-$[N(C_4H_9)_4]_2SO_4$

The electrocapillary curves for the above salts were also given. It was shown that the $\Delta\eta$ values (obtained from the $\eta$ - ln i curves) were from 0.5 to 0.7 of the shift in the electrocapillary maximums referred to the solution of $Na_2SO_4$ (an inactive electrolyte).

Iofa has pursued further the study of the effect of composition of solution on overvoltage developed on mercury electrodes. He finds that Tafel's relation is obeyed in

concentrated acid solutions but that the b-values are different from 0.12. Thus, b equals 0.140 in 3N-HCl solution, 0.124 in 5N, 0.106 in 10N, and 0.093 in 12.5N. Similar results are obtained in HBr solutions. A reasonable explanation for the above results is that the discharge process still holds but that discharge takes place from the acid molecule rather than the hydronium ion exclusively.

## Theory

### Tafel's theory.

When Tafel[34] discovered the empirical equations relating overvoltages to current densities, he immediately attempted to afford a theoretical explanation for this relationship. In this attempt he laid the foundations for the modern theory of overvoltage. Consequently, a detailed account of his hypothesis and reasoning processes will be presented here.

In the first place, Tafel assumed that the change from the hydrogen ion into the hydrogen molecule proceeded in two steps, namely:

$$H^+ + e \rightleftarrows H \qquad (1)$$

and

$$2H \longrightarrow H_2 \qquad (2)$$

Of these, he assumed the first step to be very fast as compared with the second; therefore, the second step, which he

assumed to be irreversible, was considered to be the velocity-determining process. For a stationary state, the rate at which hydrogen atoms are formed from ions must be equal to the rate at which the atoms react to form molecular hydrogen.

The former process, corresponding to equation (1), is proportional to the current density; that is,

$$dC_H/dt = k_1 i; \qquad (3)$$

whereas, reaction (2) is proportional to the concentration of hydrogen atoms raised to the power $\alpha$,

$$dC_H/dt = k_2 C_H^{\alpha} \qquad (4)$$

Therefore, the change in $C_H$ resulting from both processes may be represented by a combination of equations (3) and (4),

$$dC_H/dt = k_1 i - k_2 C_H^{\alpha} \qquad (5)$$

For a stationary state, $dC_H/dt = 0$; in this case, equation (5) reduces to

$$i = k_2/k_1 C_H^{\alpha} \qquad (6)$$

If this is substituted into Nernst's equation,

$$E = RT/F \ln C_{H^+}/C_H$$

one finally arrives at the following equation:

$$\eta = a + 2.3RT/\alpha F \log i \qquad (7)$$

in which a includes all terms that are independent of i. In

these equations, E represents the potential of an electrode where the concentration of atomic hydrogen at the electrode surface is $C_H$, and of hydrogen ions $C_{H^+}$; $\eta$ is the overvoltage (i.e., $E_R - E$); R, F, and T are the gas law constant, the value of the Faraday, and the absolute temperature, respectively. For any particular cell, $C_{H^+}$ is assumed to be constant with i.

The experimentally determined value of b in Tafel's empirical equation, at 12°C, is 0.107; the numerical value of $2.3RT/\alpha F$ is $0.057/\alpha$. Since, according to Tafel, $\alpha$ should equal 2, the experimentally determined value is practically four times as large as the theoretical value. As Tafel pointed out, this is probably due to a major mistake in the basic assumptions.

A slightly modified and improved version of Tafel's theory[14] takes into account the reverse of equation (2); i.e.,

$$H_2 \longrightarrow 2H.$$

The amount of hydrogen atoms formed by this reaction is proportional to the concentration of hydrogen molecules $C_{H_2}$.

Here, then, is obtained for the rate of decrease of $C_H$

$$-dC_H/dt = k_2 C_H^{\alpha} - k_2{}^1 C_{H_2} \qquad (8)$$

and, therefore,

$$k_1 i = k_2 C_H^{\alpha} - k_2{}^1 C_{H_2} \qquad (9)$$

Further, it can be assumed that

$$C_{H_2} = (C_{H_2})_{eq}$$

and hence, for i = o (that is, at equilibrium),

$$C_{H_2} = (C_{H_2})_{eq} = k_2/k_2^1(C_H)^{\alpha}_{eq} \qquad (10)$$

$$\text{Therefore, } k_1 i = k_2 C_H^{\alpha} - k_2(C_H)^{\alpha}_{eq} \qquad (11)$$

and, since at equilibrium $\eta$ = o,

$$i = k_3(e^{\alpha\eta(F/RT} - 1) \qquad (12)$$

or

$$\eta = 2.3RT/\alpha F \log (i + k_3) + a. \qquad (13)$$

It is readily seen that, when $i >> k_3$, this expression becomes the same as Tafel's original equation. The modified equation possesses the advantage that $\eta$ does not decrease indefinitely as i is reduced to zero. However, it still possesses two serious shortcomings, namely: (1) in most cases, the coefficient of log $(i + k_3)$ is too small; and (2) there is no theoretical basis for a, which is a constant characterizing overvoltages on different metals. In the case of very active metals, however, this equation applies nearly quantitatively. Hence, the assumption that the combination of atoms is the slow process is probably correct for active metals.

Theory of Erdey-Grúz and Volmer.

Nearly a quarter of a century later, Erdey-Grúz and Volmer[8] showed that Tafel's chief hypothesis was wrong. They used Bowden's[3] work on the beginning stage of electrolysis as a basis for their arguments. Thus, they showed that if an accumulation of atomic hydrogen is the cause of overvoltage, then the potential should increase logarithmically with growing surface concentration of hydrogen atoms. This follows from Nernst's equation:

$$\varphi = \text{const} - RT/F \ \ln C_H.$$

This relationship is not obeyed; on the contrary, $\eta$ grows linearly with the amount of electricity as long as this latter is a measure of the increase in concentration of the hydrogen species that is responsible for overvoltage. That is, the linear relationship holds until appreciable amounts of the overvoltage-active substance are lost by means of some other cause.

Experimental evidence suggests that at the beginning of electrolysis practically no hydrogen ions are discharged, but instead are adsorbed in the Helmholtz double layer; this double layer can be treated mathematically as a condenser. Therefore, the overvoltage is related linearly to the amount of electricity according to the following equation:

$$\eta = -kF\Delta(C_+ - C_-), \qquad (14)$$

where $C_+$ and $C_-$ signify the concentrations of the ions in the

double layer; here the change, $F\Delta(C_+ - C_-)$, is a measure of the quantity of electricity used to charge the condenser.

Erdey-Grúz and Volmer thus showed that the combination, process is not the hindered step in the electrolysis; probably therefore, the discharge process should be the rate-determining step. They, then, proceeded to develop a theory for a stationary state of electrolysis.

If U is the necessary activation energy for the transfer of an electron from the metal to the hydrogen ion, then the number of neutralizations taking place per second is

$$N_o = k_1' C_{H^+} e^{-U/RT} \qquad (15)$$

where $k_1'$ is a constant and $C_{H^+}$ is the concentration of hydrogen ions of the electrode surface; the subzero on the N refers to the condition that the electrode is at its zero or "null" potential with respect to the electrolyte. If, however, a potential difference, E, exists between the electrode and solution in the sense that the electrode is positively charged with respect to the solution, then the transfer of an electron from the metal to the ion will be hindered; that is, the activation energy will be raised by an amount $\alpha EF$, where $\alpha < 1$. The number of neutralizations per second in this case is

$$N_E = k_1' C_{H^+} e^{-(U + \alpha EF)/RT} = k_1 C_{H^+} e^{-\alpha EF/RT} \qquad (16)$$

The reverse process, namely the electron transfer from a

neutral hydrogen atom to the metal, takes place in an analogous fashion; therefore, the number of ionizations per second is

$$N_H = k_2' C_H e^{-(W - \beta EF)/RT} = k_2 C_H e^{\beta EF/RT} \qquad (17)$$

At the equilibrium potential, $E_R$, $N_E = N_H$. For this reason,

$$C_H = k_3 C_{H^+} e^{-(\alpha + \beta)EF/RT} \qquad (18)$$

But from Nernst's equation,

$$C_H = k_4 C_{H_1^+} e^{-E_R F/RT} \qquad (19)$$

where $C_{H_1^+}$ is the concentration of hydrogen ions in the body of the solution; that is,

$$k_3 C_{H^+} e^{-(\alpha + \beta)E_R F/RT} = k_4 C_{H_1^+} e^{-E_R F/RT} \qquad (20)$$

That $C_{H^+}$ varies linearly with $C_{H_1^+}$ seems evident; moreover, it is probable that $C_{H^+}$ varies with $E_R$. That this latter variation is negligible as compared with the variation of the exponential in $E_R$ results from the following arguments. First, it is known that the potential varies linearly with the increase of excess of positive ions over negative ions at the electrode; second, for an increase of 100 mv an increase of only 1/3000 part of a layer of hydrogen ions is necessary; third, an increase of 100 mv corresponds to an increase of $e^{E_R F/RT}$ by a factor of more than 50. From these facts, it follows that the increase in total hydrogen

concentration at the surface is surely much less than linear with the potential, particularly whenever the experiments are carried out in the usual solutions containing from 0.1 to 1 mole/liter of acid. Therefore, since $C_{H^+}$ can be assumed to be constant as compared with $e^{-(\alpha+\beta)E_R F/RT}$, then

$$\alpha + \beta = 1 \tag{21}$$

If a potential E, different from $E_R$ by an amount $\eta$, is applied then,

$$N_E - N_H = i/F = k_1 C_{H^+} e^{-\alpha(E_R - \eta)F/RT} - k_2 C_H e^{\beta(E_R-\eta)F/RT} \tag{22}$$

or

$$i = k_5 C_{H^+} e^{+\alpha\eta F/RT} - k_6 C_H e^{-\beta\eta F/RT} . \tag{23}$$

Since, with increasing polarizations, the second term becomes progressively smaller ($\eta > 0$), it can be neglected as compared with the first when the potential is at some distance from the reversible ($\sim 0.03$ volt):

$$i = k_5 C_{H^+} e^{+\alpha\eta F/RT} \tag{24}$$

Or, since $C_{H^+}$ is, relatively speaking, a constant,

$\eta = a + b \log i$ with

$$b = 2.3RT/\alpha F; \tag{25}$$

since, experimentally, $b = 0.116$, then $\alpha = 0.5$. Thus, $\alpha = \beta$, which is not unreasonable inasmuch as it implies that the applied potential is distributed equally to the activation potentials of the neutralization and ionization processes, respectively.

Gurney's theory.

Gurney[18,19], starting with a different viewpoint, arrived at a theory that, upon further elaboration, amounts to essentially the same as Volmer's theory. However, his theory refers explicitly to known quantities such as ionization energy, hydration energy, and the thermionic work function of metals; whereas, in the Volmer theory, the corresponding quantities appear grouped together in a somewhat vague activation energy. For this reason, it is desirable to set forth the essential points of the Gurney theory.

Gurney first examined a system composed of a metal and a proton in a vacuum. To the metal he assigned a thermionic work function, $\Phi$; to the proton, an ionization energy, J. That is, an electron requires additional energy amounting to $\Phi$ before it can leave the metal; and it loses energy amounting to J when it unites with a proton. These conditions are schematically represented by Figures 7 and 8, respectively.

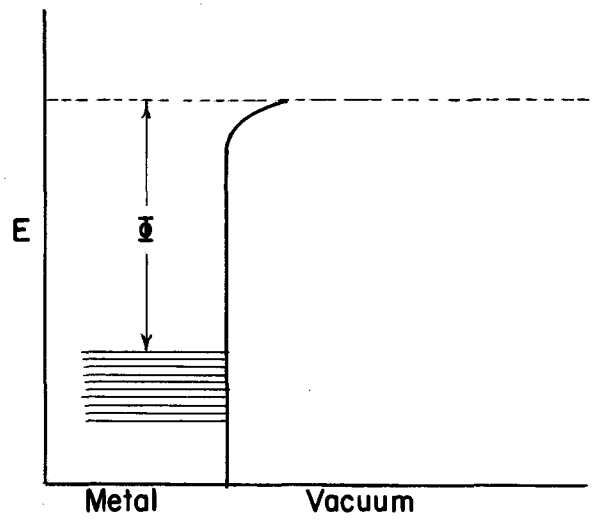


Fig. 7. Energy of the electron in the metal. The striped region shows the energy states filled with electrons.

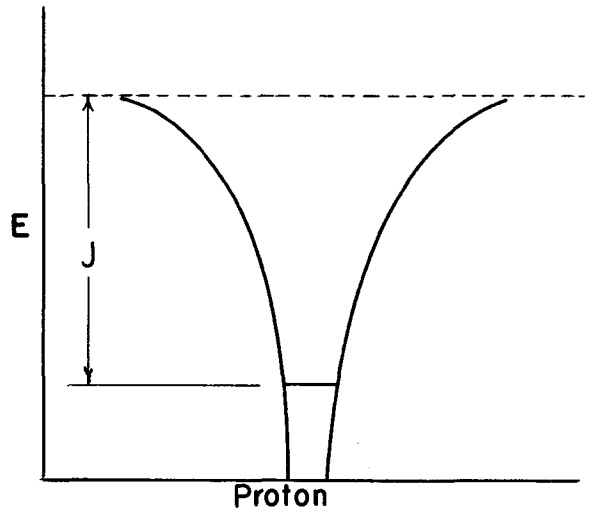


Fig. 8. Energy of an electron in the neighborhood of a proton. The horizontal line represents the ground level of the electron.

In order to combine the two figures, a common level of energy must be found. The energy of the free electron serves this purpose; it is used in Figures 7, 8, and 9 as the basis of the energy of the electron.

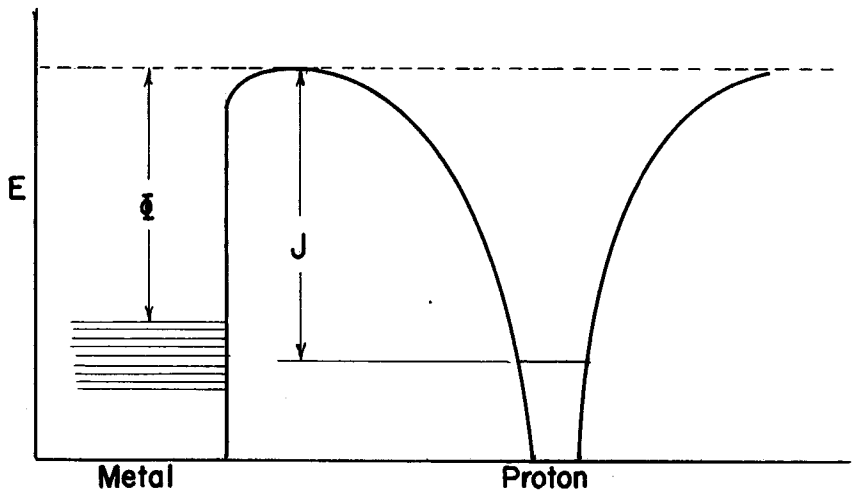


Fig. 9. Schematic representation of the discharge of a proton near a metal.

The classical mechanics forbids the passage of an electron from the metal to the proton because of the intervening potential barrier. Gurney, however, shows that quantum mechanics allows the transition of an electron from the metal to a proton even at a distance of several molecular diameters. This is, of course, further dependent upon the condition that $J > \Phi$.

In an aqueous solution a somewhat different set of conditions prevails. The proton is replaced in the problem by an hydronium ion, $H_3O^+$, which may be more or less hydrated. Thus, when the hydronium ion is neutralized by an electron, a certain amount of energy (which may be designated the

neutralization energy $E_0$) will be liberated. This neutralization energy will be less than the ionization energy by an amount equal to the hydration energy; this latter is the amount of energy required to replace that lost by the proton when it reacted with water to form the hydrated hydronium ion. The energy relationships are shown in Figure 10.

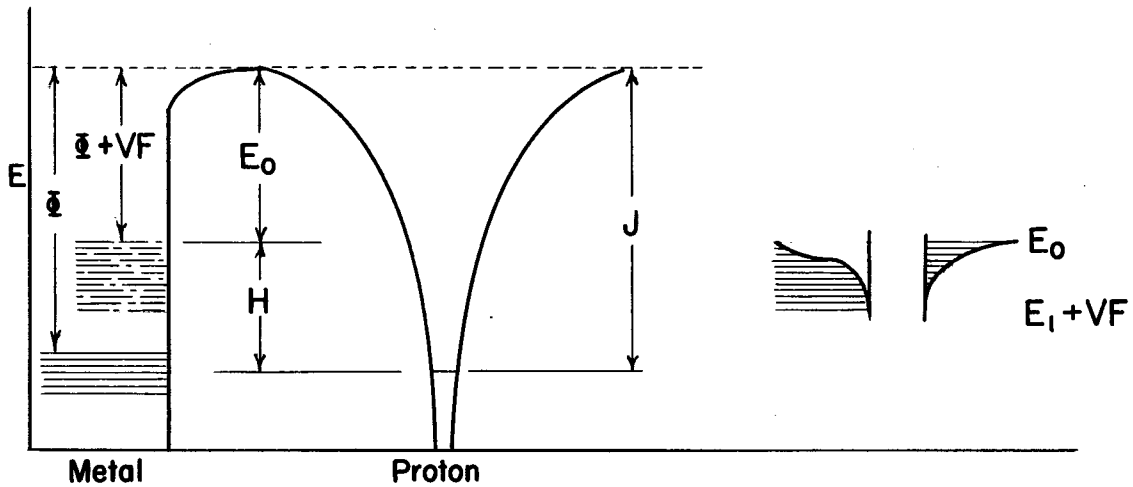


Fig. 10. Energy-relationships for the discharge of a hydrated proton.




Fig. 11. Schematically showing distribution of electrons in the energy levels of metal and ion.

In the situation as pictured in Figure 10, it is evident that the hydrated proton can no longer be discharged although the unhydrated proton could have been. In order for the discharge to occur, energy must now be supplied to the metal electron; in Figure 10 this corresponds to VF. The additional energy may be supplied by applying an outside source

of potential; in that case, V represents the applied potential.

Actually there will be a temperature distribution of energy for the ions in the solution and for the electrons in the metal (schematically shown in Figure 11). The energy distribution for the ion, N(E), may be represented by means of the Boltzmann law,

$$N(E) = N_o \, e^{(E - E_o)/RT}$$

The distribution among the electrons, n(E), obeys the Fermi-Dirac law which can be approximated to a Boltzmann distribution,

$$n(E) = n_o \, e^{-[E - (E_1 + VF)]/RT}$$

The significance of E can be understood from reference to Figures 10 and 11. Classically, a transition of an electron in either direction would be forbidden by an energy barrier; quantum-mechanically, however, there exists a finite probability that such a transition can occur. The important term of the probability function, P(E), is also an exponential,

$$P(E) = e^{-4\pi x\sqrt{2mE}/h}$$

where x is the mean thickness of the energy barrier, h is Planck's constant, and m is the mass of the electron.

The number of discharges, and hence the current density also, is proportional to the integral over the product of the two distributional and the probability functions.

$$i \sim \int_{E_1 + VF}^{E_o} N(E) \cdot n(E) \cdot P(E)\, dE$$

This integral leads to a relationship that is very similar to Tafel's equation, but does not as yet contain the factor $\alpha$. The theory has been expanded in order to include this factor.

In the primitive form, Gurney tacitly assumed that the mutual potential of a hydrogen atom and water molecule is zero. This is not so, and in his revised theory he takes into account the positive potential which exists in the system immediately after neutralization. The energy relationship may be understood quite easily if reference is made to Figure 12.

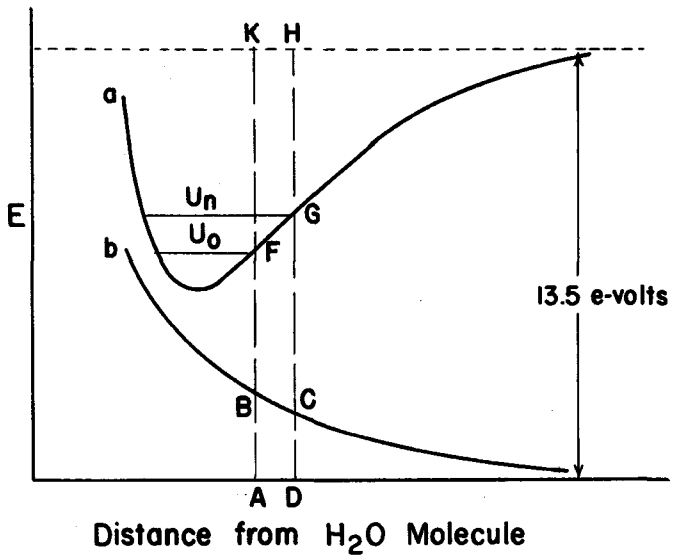


Fig. 12. Energy relationships showing how repulsion between electron and H-atom leads to the factor $\alpha$.

Here curve "a" represents the potential energy of a system composed of a proton and water molecule; curve "b" shows the potential energy of a hydrogen atom and a water molecule. If neutralization of the hydrogen ion occurs in its lowest vibrational-rotational state, $U_o$, then the energy of neutralization, $E_o$, will be that pictured by FB; at a higher vibrational-rotational energy level, $U_n$, the neutralization energy, $E_n$, can be represented by GC. It is seen that

$$E_n - E_o = \gamma(U_n - U_o)$$

where $\gamma$ is a factor greater than one; in the special case that the slopes have equal magnitudes but opposite signs, $\gamma = 2$.

The correct distribution function for the ions must be a function of its own energy; thus,

$$N(U) = N_o\, e^{(U - U_o)/RT} = N_o\, e^{(E_n - E_o)/\gamma RT}$$

When this distribution function replaces the previous one in the integral, a relationship is now obtained that includes the factor $\alpha$ in the form of $1/\gamma$. The evaluation of the integral when all unimportant terms are dropped gives:

$$\log i = (E_o - E_1 + VF)/\gamma RT + \log T + \text{const.}$$

When this equation is differentiated with respect to V and T, two equations are obtained, respectively,

$$d(\log i)/dV = F/\gamma RT$$

and

$$d(\log i)/dT = (E_1 - E_o - VF)/\gamma RT^2 + 1/T$$

where $\gamma$ is greater than 1.

If $\gamma$ is assigned the not unreasonable value of two, the first equation is in excellent accord with experimental findings. Thus, it is in agreement with these facts: (1) the current density is increased by a factor of ten when the applied voltage is increased by 0.12 at room temperature; and (2) the amount the applied voltage must be increased is directly proportional to the temperature for similar increases in the current densities.

The second equation corresponds to experimental results nearly as satisfactorily as the first. The qualitative finding that d(log i)/dT decreases as the applied voltage increases is verified; even the quantitative relationship is closely approached if a correct estimate was made of the range of neutralization energies over which the integral was taken.

Thus far in the discussion of Gurney's theory no consideration has been given to the reversible reaction. That is, the process of deposition alone has been considered. This is justifiable in the case of high-overvoltage metals but in the instance of low-overvoltage metals, such as platinized platinum, the ionization process must also be taken into account. Butler[6] has completed the theory by fusing those of Gurney and of Horiuti and Polanyi[7] into one that includes

the reversible hydrogen electrode as a special case.

The antisymmetrical relationship that exists between the overvoltage and the ability of a metal to absorb hydrogen has been mentioned. This property suggests that absorbed hydrogen has a lower energy of activation than "free" hydrogen in the discharge process. This lower activation energy may allow for the attainment of a considerable rate for the ionization process; that is, the ionization reaction may become fast enough so that the reverse process (the discharge reaction) may even be helped by the passage of an electric current without requiring any large added potential. In other words, the rates of the ionization and discharge reactions are so great at equilibrium that small disturbances, corresponding to small currents, requires but relatively small causative potentials.

Butler attacked the particular case for nickel since this metal has strong adsorbing powers for hydrogen. He found an activation energy of 8 k. cal. for the most probable configuration of the nickel atom, the hydronium ion, and the proton. According to measurements of Bowden, the transfer rate of protons from the ionic side is $10^{-5}$ amps/cm$^2$, when the activation energy is 10 k. cals. Hence, at the reversible potential, the reactions are occurring at rates equivalent to $2.5 \times 10^{-4}$ amps/cm$^2$. It is evident, therefore, that appreciable currents may be caused to pass without any large displacement from the equilibrium potential.

Frumkin addition to Volmer theory.

Frumkin[10,11,31] has enlarged upon Volmer's theory by considering the structure of the double layer. Volmer tacitly assumed a sharp non-diffuse Helmholtz double layer. Frumkin, however, makes use of the Stern theory[33] of the double layer; that is, he assumes a Gouy diffuse layer added to the Helmholtz non-diffuse layer. It will be recalled, also, that in the Erdey-Grúz and Volmer theory the concentration of the hydrogen ions in the double layer, $C_{H^+}$, is assumed to be roughly proportional to the concentration of the hydrogen ions in the body of the liquid, $C_{H_1^+}$. This assumption was sufficiently accurate for their purpose, but Frumkin has developed an elaboration upon their theory based on a relationship that probably exists between $C_{H^+}$ and $C_{H_1^+}$.

He designated with $\varphi$ the mean potential (potential in interior of liquid equal to zero) in the plane that passes through the centers of the ions in immediate contact with the surface of the electrode. He assumed that these ions were the only ones discharged. But, according to Erdey-Grúz and Volmer, the discharge velocity is proportional to

$$C_{H^+}\, e^{-\alpha\varphi F/RT},$$

where $\varphi$* is the potential difference electrode-electrolyte and $\alpha$ is a fraction. If the part of $\varphi$ that acts across the

* $\varphi$ is the same as the E used in Tafel's and Erdey-Grúz and Volmer's derivations.

Helmholtz layer is designated by $\psi$, the following expression is now obtained for the discharge velocity:

$$k_1 \, C_{H^+} \, e^{-\alpha\psi F/RT}$$

But, $C_{H^+}$ is related to $C_{H^+_1}$ by means of $\zeta$ according to the equation

$$C_{H^+} = C_{H^+_1} \, e^{-\zeta F/RT}$$

hence, the number of ions discharging per second is

$$k_1 \, C_{H^+_1} \, e^{-\alpha\psi F/RT} \, e^{-\zeta F/RT}$$

The number of hydrogen atoms ionizing per second is given by

$$k_2 \, C_H \, e^{\beta\psi F/RT}$$

At the reversible potential, the two expressions are equal; therefore, setting them equal and simplifying,

$$(\alpha + \beta)\psi_R + \zeta_R = RT/F \ \ln C_{H^+}/C_H + \text{const.}$$

It follows that $\alpha + \beta = 1$; (since $\psi_R + \zeta_R = \varphi_R$, and $\varphi_R = RT/F \ \ln C_{H^+}/C_H$). Therefore, if the logical assumption is made that $\alpha = \beta$, then, $\alpha = \frac{1}{2}$, and

$$k_1 \, C_{H^+_1} \, e^{-\psi F/2RT} \, e^{-\zeta F/RT} = k_1 \, C_{H^+_1} e^{-\psi F/2RT} \, e^{-\zeta F/2RT}$$

From this expression, which is proportional to the current density whenever the ionization reaction is negligible, the following equation is obtained:

$$\varphi + \zeta = 2RT/F \ln C_{H^+_1} - 2RT/F \ln i + \text{const.}$$

This equation, at constant hydrogen-ion concentration, reduces to

$$\varphi + \zeta = -2RT/F \ln i + \text{const.}$$

It differs, therefore, from Erdey-Grúz and Volmer's expression

$$\varphi = -2RT/F \ln i + \text{const.}$$

since $\zeta$ is a function of $\varphi$. However, at the potentials that come into use in overvoltage measurements and in not too dilute solutions, $\zeta$ does not vary with $\varphi$ outside of the experimental limits of error in measuring $\varphi$. Therefore, $\zeta$ can be treated as a constant with respect to $\varphi$ within these limitations. It is only in the neighborhood of the electrocapillary maximum, especially in dilute solutions, that the variation of $\zeta$ must be considered.

The general equation, with constant current density, reduces to

$$\varphi + \zeta = 2RT/F \ln C_{H^+_1} + \text{const.}$$

It is this equation that can be used to explain the effect of the composition of electrolyte on overvoltage.

Frumkin distinguished two cases:

(1) The investigations were carried out in the presence of a large excess of a foreign electrolyte, so that $\zeta$ remained

constant with changing hydrogen-ion concentration. In this case, $\varphi$ changes by an amount 0.116 with tenfold decrease in the $H^+$-ion concentration. Inasmuch as $\varphi_R$ changes only 0.058 with the same decrease, according to Nernst's theorem, then $\eta$ (i.e., $\varphi_R - \varphi$) is changed 0.058 whenever the $H^+$-ion concentration is reduced tenfold. This conclusion has been confirmed by experiments of Herasymenko and Šlendyk; experiments conducted by Bowden at moderate current densities also confirmed the above conclusion, but tests at low-current densities revealed no effect on overvoltage of changing $H^+$-ion concentration.

(2) If the dilution of the acid is carried out in the absence of foreign electrolytes, $\zeta$ varies with the dilution. This variation, in moderate concentrations, can be expressed according to Stern's theory by the equation

$$\zeta \sim RT/F \ln C_{H^+_1} + \text{const.}$$

Hence

$$\varphi = RT/F \ln C_{H^+_1} + \text{const.}$$

This explains, therefore, why $\eta$ is independent of variations in $H^+$-ion concentration in pure solutions of acids.

# EXPERIMENTAL

## Choice of Method

In the past there have been two general procedures used in the pursuance of overvoltage data, namely: (1) the direct method and (2) the commutator method. In the direct method the potential of the electrode in question is measured while current is flowing in the electrolyzing cell; whereas, in the commutator method the current is stopped during the measuring interval. The direct method is objected to on the basis that the potential measurement includes a so-called "transfer resistance" drop (which is, therefore, not an electromotive force); and since this "transfer resistance" is supposed to amount to several thousand ohms, the voltage drop due to it may be quite large. However, investigations by Tartar and Keyes[35], Knobel[26], and Glasstone[14,15,17] tend to rule out the existence of any such resistance of magnitude more than a few ohms. A lengthy (fifteen years) and exhaustive comparison of the two methods has been carried out by Ferguson and his co-workers. Ferguson[9] has recently published a short review of this work in which the direct method is shown to be superior to the commutator method in that the latter possesses several inherent sources of error.

It was shown also that the direct method could be relied upon to give true overvoltages. Hence this method was chosen.

## Apparatus and Materials

A diagram of the apparatus used appears on the following page. The arrangement is a standard one that appears frequently in the scientific literature and textbooks and, therefore, no detailed description of it will be given. A Leeds and Northrup Student Type potentiometer was found to give sufficiently precise measurements for the purposes of this work. The standard reference cell was one that had been made by a student as a laboratory exercise but it was checked periodically against a primary standard belonging to the Physical Chemistry department. Its potential was found to be sufficiently constant (within 0.0002 v for three checks in a six-month period). The source of the electrolyzing potential was a battery of lead storage cells having a potential of 120 v.

The electrolyzing cell is shown in detail in Figure 14. It was made from Pyrex glass by a local glassblower. The connecting sidearm was first made of capillary glass. However, this arrangement was found to be unsatisfactory for the reason that minute bubbles of gas collecting in the passageway would stop the electrolyzing current. For this reason, a larger connection was necessary, and diffusion was hindered by the simple expedient of filling the tube with surgical

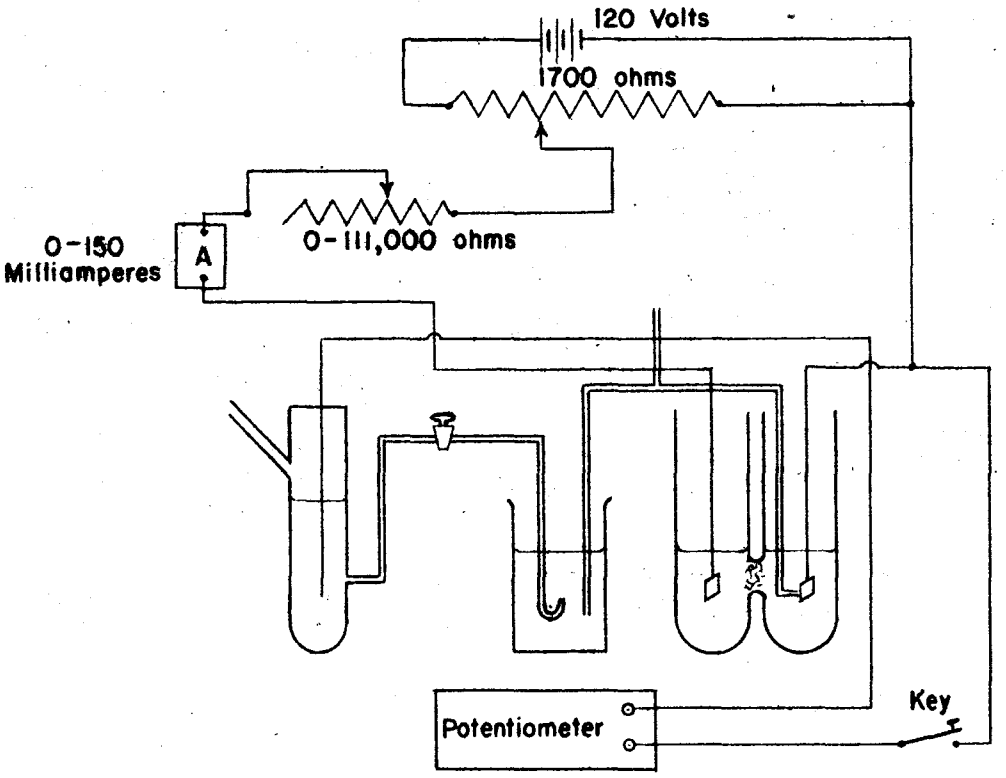


Fig. 13 Diagram of Apparatus for Polarizing and Measuring Circuits

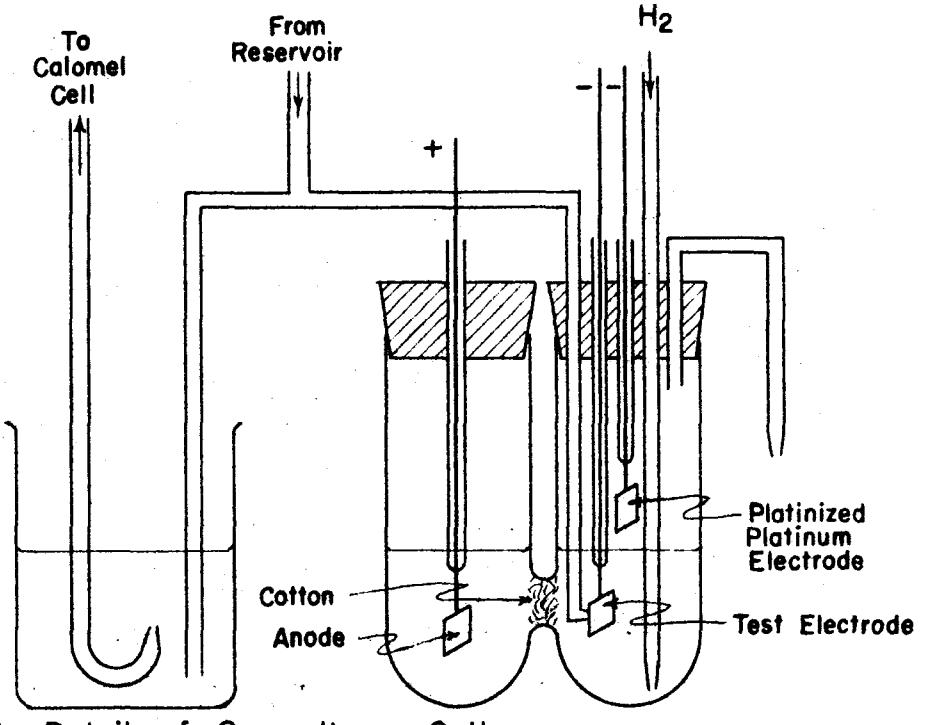


Fig. 14 Detail of Overvoltage Cell

cotton batting. Check runs were made in 2N-NaOH and 0.2N-NaOH in order to determine if the presence of the cotton affected the overvoltage; that is, three runs on each of these two solutions were made--the first with no cotton in the tube, the second immediately after filling the cell with the electrolyte and with cotton in the tube, and the third after allowing the cotton to remain in contact with the solution for twelve hours. The results from the second and third runs were practically identical and nearly the same as those of the first; moreover, the former were more easily reproduced. That the cotton had no injurious effects on the measurements was evident, therefore.

The use of an exterior source of hydrogen for saturating the solution with hydrogen was found to be not absolutely necessary. It was used, however, for its stirring effect in order to reduce concentration-polarization effects and to maintain an even concentration throughout the solution. The vent tube from the cathode compartment acted to maintain the hydrogen atmosphere above the solution and to vent off the hydrogen coming from the electrolysis and the exterior source. A droplet of liquid in the capillary part of this tube acted as an effective valve for preventing the entrance of air into this compartment. A tank of electrolytic hydrogen served as a source of the hydrogen, which was purified by passage through two gas-wash bottles containing alkaline pyrogallol and a third containing distilled water.

The electrode was made from a small piece of electrolytic iron which was spectroscopically pure except for traces of copper. One side was filed and then polished with various grades of emery cloth in order to obtain a smooth surface; the other side was covered with solder and attached to a chromel wire. The chromel wire was then sealed into a glass tube, and it and the soldered back of the electrode were covered with a methacrylate plastic coating. The coating was allowed to set for two days before using the electrode. Electrical connection was made by means of mercury in the glass tube.

Electrolytic connection to the saturated calomel reference electrode was made by means of a salt bridge filled with the solution under consideration. This bridge was drawn out to a fine capillary tip[27] 0.5 mm in diameter which in operation was pressed tightly against the test electrode. The bridge was so constructed as to make possible the easy creation of a siphoning effect. This was done in order to fill the bridge directly from the cathode compartment and thus minimize the chances that foreign material might enter the cell. The other end of the bridge dipped into a small beaker that contained a small amount of the solution under consideration; the sidearm of the calomel cell also dipped into this solution.

The chemicals used were reagent grade and were not specially purified. For dilution water from the distilled

water tap was used. However, the NaOH solution was made by first preparing a saturated solution in specially distilled water. The suspended matter was allowed to settle and the supernatant liquid allowed to siphon into a bottle of the specially distilled water. A titration on the resulting solution gave its strength; it was then further diluted to 2.00N within one point in the second decimal place. This solution was stored in a bottle equipped with a siphon and a lime-soda tube.

The above solution was used directly for the run using plain 2N-NaOH solution; and whenever erratic readings indicated that the electrode required checking, repeat runs were made using this solution. The 0.2N-NaOH solutions were made by diluting 25 ml of the stock solution to 250 ml, and the 0.02N-NaOH solutions were made by diluting the latter solution similarly. The solutions in which the added salt concentrations were 2N were made by weighing the calculated amount of the salt to the nearest decigram and adding it directly to the 2N-NaOH solution. Thus these solutions were slightly weaker than 2N in NaOH; however, the 0.2N- and 0.02N-NaOH solutions had the correct base concentration since these were made by using 25 ml of the stock solution and the calculated weight of the salt and diluting to 250 ml. The weaker salt solutions were made by appropriate dilutions with either 2N-, 0.2N-, 0.02N-NaOH solution or water as required.

## Method of Procedure

The cell, electrodes, and auxiliary parts were thoroughly cleaned before each run. The cell and its glass auxiliary parts were rinsed with sodium chromate-sulfuric acid cleaning solution; this was flushed off using a freely flowing stream of tap water, and finally, the apparatus was rinsed two or three times with distilled water. The platinum electrodes were usually cleaned using only a fine stream of distilled water; occasionally, the iron electrode was cleaned with hot NaOH solution and rinsed with distilled water and the platinum electrodes by dipping them into concentrated nitric and hydrochloric acids alternately with intermediate rinsings of distilled water. Several different kinds of treatment were tried for the iron electrode, but the treatment which proved to be most satisfactory turned out to be the simplest. The surface of the iron was simply polished with No. 00 emery paper for twice as long as any evidence of previous staining or pitting was visible. The surface was then washed vigorously with distilled water and finally was rinsed with the solution to be used in the test run. All this was done immediately before placing the electrode in the solution.

The cell was then half-filled with the solution to be tested. The rubber stoppers holding the electrodes and auxiliary equipment were put into place and the hydrogen source was turned on so that a fine stream of bubbles passed

up through the solution. At the beginning of a run the platinized platinum electrode was suspended above the solution, inasmuch as traces of platinum have been found to affect the overvoltage developed on a mercury surface[32]; hence, it was deemed advisable not to have a platinized surface too close to the test iron electrode in the same solution.

From this point on a variety of procedures were followed, which in the following will be designated as Procedures A, B, and C.

In Procedure A, the current was adjusted to $10^{-4}$ ampere and the potential of the electrode allowed to approach a nearly stationary state (that is, the potential did not increase more than one millivolt per minute). The potential was determined, and then the current was increased to one milliampere, the potential allowed to approach a stationary value again, and finally it was determined and recorded. Thus the values for ascending amounts of current were determined. Each time the descending values were determined also; and, as a check, the entire Procedure A was repeated. Invariably, the values determined from the rerun were higher than the first values.

In Procedure B, a preliminary current amounting to one-tenth ampere was passed for five minutes. The current was then shut off for five minutes and the potential determined. Here, again, both ascending and descending values of the

potential were determined twice.

In Procedure C, the preliminary current was only one-hundredth ampere. This current was allowed to flow for five minutes; it was then shut off, and after five minutes the potential was read. The current was increased again stepwise and the potential read, but now this was done as quickly as it was feasible to do so. Ascending and descending values were determined twice. Procedure C was used in most of the trials that yielded worthwhile results.

The purpose of each of these procedures was to furnish a standard method so that trials on different solutions could be compared. It was necessary to make the time intervals nearly equal in a series of trials inasmuch as the overvoltage developed on iron electrodes rises continuously with time. Since only the difference between the comparable overvoltages obtained in a series of runs was desired, it was permissible to measure the overvoltage in this fashion. Procedure C was adopted for the greater number of the tests because the method was the least time-consuming and therefore the electrode surface would be least affected.

## Discussion of Results

### Effect of concentration of NaOH.

Typical sets of data as gathered in the laboratory are presented in Table 8. The data were obtained according to

Table 8

Effect of NaOH-Concentration on Overvoltage
(Electrode area = 2.25 $cm^2$)

| Current (in ma) | Concentration of NaOH | | | | | |
|---|---|---|---|---|---|---|
| | 2N | | 0.2N | | 0.02N | |
| | $\varphi$ | $\eta$ | $\varphi$ | $\eta$ | $\varphi$ | $\eta$ |
| 0 | 1.139 | 0.075 | 1.059 | 0.049 | 1.089 | 0.132 |
| 0.1 | 1.181 | 0.115 | 1.143 | 0.133 | 1.110 | 0.153 |
| 1 | 1.358 | 0.292 | 1.315 | 0.305 | 1.305 | 0.348 |
| 10 | 1.505 | 0.439 | 1.450 | 0.440 | 1.463 | 0.506 |
| 100 | 1.620 | 0.554 | 1.558 | 0.548 | 1.569 | 0.612 |
| 150 | 1.640 | 0.574 | 1.589 | 0.579 | 1.602 | 0.645 |
| 100 | 1.625 | 0.559 | 1.573 | 0.563 | 1.583 | 0.626 |
| 10 | 1.500 | 0.434 | 1.470 | 0.460 | 1.457 | 0.500 |
| 1 | 1.368 | 0.302 | 1.322 | 0.312 | 1.317 | 0.360 |
| 0.1 | 1.207 | 0.141 | 1.172 | 0.162 | 1.133 | 0.176 |
| 0 | 1.145 | 0.079 | 1.043 | 0.033 | 1.085 | 0.128 |
| Plat. Pt. | 1.066 | | 1.010 | | 0.957 | |

Table 9

Overvoltage-Concentration Data at Constant Current

| Current (in ma) | Concentration of NaOH | | | | |
|---|---|---|---|---|---|
| | 2N | | 0.2N | | 0.02N |
| | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ |
| 0.1 | 0.115 | 0.018 | 0.133 | 0.020 | 0.153 |
| | 0.141 | 0.021 | 0.162 | 0.010 | 0.176 |
| 1 | 0.292 | 0.013 | 0.305 | 0.043 | 0.348 |
| | 0.302 | 0.010 | 0.312 | 0.048 | 0.360 |
| 10 | 0.439 | 0.001 | 0.440 | 0.066 | 0.506 |
| | 0.434 | 0.026 | 0.460 | 0.040 | 0.500 |
| 100 | 0.554 | -0.006 | 0.548 | 0.064 | 0.612 |
| | 0.559 | +0.004 | 0.563 | 0.063 | 0.626 |

Procedure B, but very similar data were obtained by Procedure C, which will not be given here. The potential of the test electrode, referred to the saturated calomel electrode, is represented by $\varphi$ and the overvoltage by $\eta$. The latter is obtained by subtracting from $\varphi$ the reversible potential which was obtained by means of the platinized platinum electrode. In Table 9 these same data are rearranged and presented in a way to emphasize the shift in overvoltage on tenfold dilution. The data from Tables 8 and 9 are shown graphically in Figures 15 and 16, where ascending values only are plotted. However, both ascending and descending data are shown in Table 9 where the former is the upper value and the latter the lower for the given value of current. Despite the considerable variance in the individual values for overvoltage in these two sets of $\eta$'s, there is good accord between the respective $\Delta\eta$'s.

The results presented here are admittedly only qualitative in character; hence, conclusions drawn from them are to be considered of the same nature. Nevertheless, there is good agreement between the value of 2.3RT/F and the values of $\Delta\eta$ at the higher-current densities on tenfold dilution from 0.2N to 0.02N-NaOH concentrations. This is in good agreement with the results obtained by Lukovtsev, Levina, and Frumkin on nickel electrodes. Their results show, on the other hand, a like shift in overvoltage on dilution in solutions of NaOH as concentrated as 8.8N. Further, the same shift was observed down to current densities of $10^{-6}$ amp/cm$^2$.

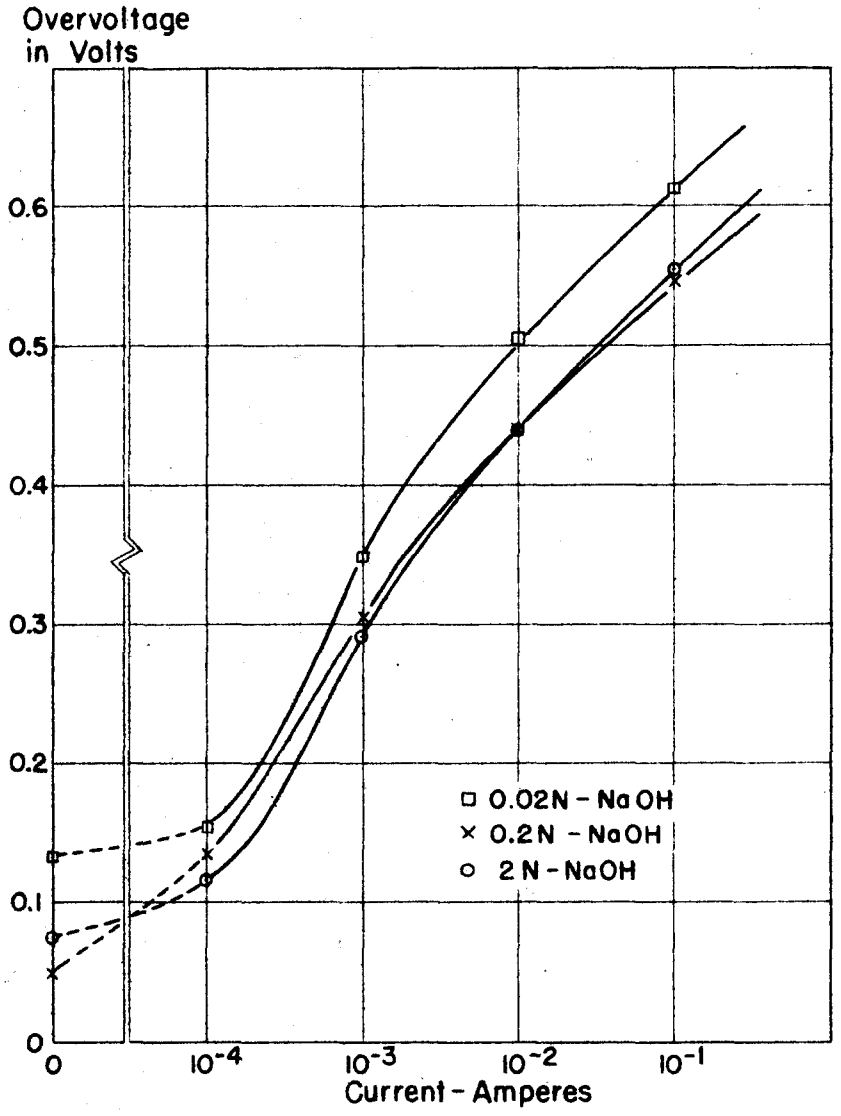


Fig. 15 Effect of Concentration of Na OH on Overvoltage-Current Density Curves

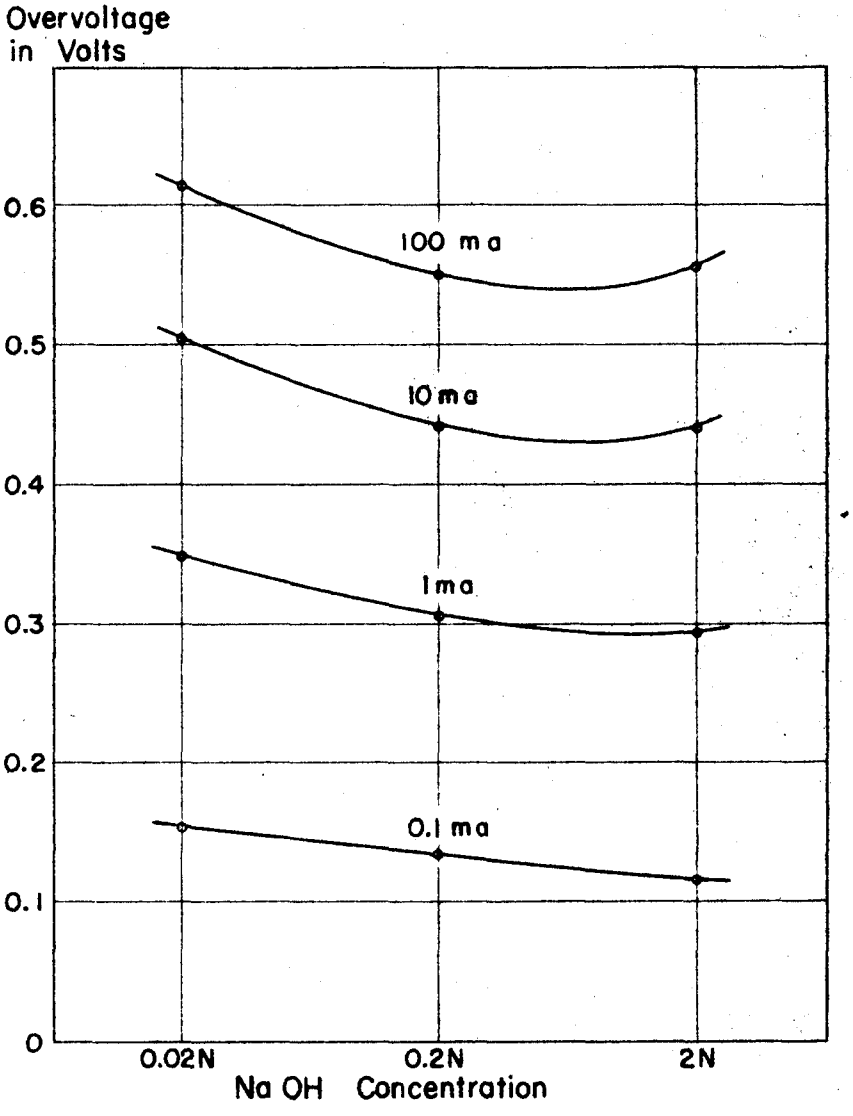


Fig. 16 Overvoltage - Concentration Curves at Constant Current Density

Effect of adding $Na_2SO_4$ to pure NaOH solutions.

Data obtained from measurements in 2N-NaOH solutions with added concentrations of 0.02N-, 0.2N-, and 2N-$Na_2SO_4$ were converted into $\eta$ and $\Delta\eta$ values. These results are presented in Table 10, where now $\Delta\eta$ signifies the difference in the $\eta$'s of the pure alkali solution and the $\eta$'s of the added-salt solutions.

Table 10

Effect of Added $Na_2SO_4$ on Overvoltage in 2N-NaOH Solutions.

| Current (ma) | Concentration of Added $Na_2SO_4$ | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 0.02N | | 0.2N | | 2N | |
| | $\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ |
| 0 | 0.071 | 0.080 | +0.009 | 0.072 | +0.001 | 0.072 | +0.001 |
| | 0.077 | 0.067 | -0.010 | 0.067 | -0.010 | 0.063 | -0.014 |
| 0.1 | 0.096 | 0.108 | +0.012 | 0.098 | +0.002 | 0.100 | +0.004 |
| | 0.115 | 0.121 | +0.006 | 0.105 | -0.010 | 0.110 | -0.005 |
| 1 | 0.188 | 0.181 | -0.007 | 0.185 | -0.003 | 0.185 | -0.003 |
| | 0.166 | 0.173 | +0.007 | 0.167 | +0.001 | 0.173 | +0.007 |
| 10 | 0.325 | 0.321 | -0.004 | 0.312 | -0.013 | 0.321 | -0.004 |
| | 0.328 | 0.320 | -0.008 | 0.317 | -0.011 | 0.332 | +0.004 |
| 100 | 0.466 | 0.441 | -0.025 | 0.432 | -0.034 | 0.433 | -0.033 |
| | 0.481 | 0.448 | -0.033 | 0.442 | -0.039 | 0.442 | -0.039 |

The table shows the results clearly enough not to require a figure to do so. Thus it is clear that the added salt has no effect on overvoltage except possibly at the highest

current density (the value for the NaOH solution may have been in error).

When $Na_2SO_4$ is added to 0.2N-NaOH solutions, the results are otherwise. The data are summarized in Table 11 and are shown graphically in Figure 17. These show that there is a consistent increase in overvoltage at the lower current densities as the concentration increases. At the higher current densities, however, there is a maximum in the curve when the concentration of the added salt equals the base concentration. At the highest current density and the largest concentration there is an actual decrease in overvoltage. The same results can be observed from inspection of Table 12 and Figure 18, which contain the data from experiments using 0.02N-NaOH and added $Na_2SO_4$.

Effect of altering NaOH concentration with constant $Na_2SO_4$ concentration.

The data from the 2N-$Na_2SO_4$ columns in Tables 10, 11, and 12 are arranged in a different way and shown graphically in Figure 19. The qualitative aspects of Figure 19 are seen to be in general agreement with those of Figure 16. A depressing effect by the $Na_2SO_4$ may be noted on the lowest NaOH concentration, particularly at the lower current densities. The figures are, however, not strictly comparable, since the data for them were not obtained by the same procedures.

Table 11

Effect of Added $Na_2SO_4$ on Overvoltage in 0.2N-NaOH Solutions

| Current (ma) | Concentration of Added $Na_2SO_4$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 0.02N | | 0.2N | | 2N | |
| | $\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ |
| 0 | 0.012 | 0.026 | 0.014 | 0.050 | 0.038 | 0.067 | 0.055 |
| | 0.009 | 0.031 | 0.022 | 0.061 | 0.052 | 0.073 | 0.064 |
| 0.1 | 0.100 | 0.105 | 0.005 | 0.111 | 0.011 | 0.118 | 0.018 |
| | 0.115 | 0.125 | 0.010 | 0.135 | 0.020 | 0.119 | 0.004 |
| 1 | 0.209 | 0.213 | 0.004 | 0.221 | 0.012 | 0.208 | -0.001 |
| | 0.189 | 0.200 | 0.011 | 0.207 | 0.018 | 0.185 | -0.004 |
| 10 | 0.332 | 0.335 | 0.012 | 0.343 | 0.011 | 0.332 | 0.000 |
| | 0.331 | 0.341 | 0.010 | 0.346 | 0.015 | 0.337 | 0.006 |
| 100 | 0.435 | 0.436 | 0.001 | 0.435 | 0.000 | 0.422 | -0.013 |
| | 0.444 | 0.446 | 0.001 | 0.444 | 0.000 | 0.431 | -0.013 |

Table 12

Effect of Added $Na_2SO_4$ on Overvoltage in 0.02N-NaOH Solutions

| Current (ma) | Concentration of Added $Na_2SO_4$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 0.02N | | 0.2N | | 2N | |
| | $\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ | $\eta$ | $\Delta\eta$ |
| 0 | 0.000 | 0.023 | 0.023 | 0.046 | 0.046 | 0.052 | 0.052 |
| | 0.002 | 0.038 | 0.036 | 0.068 | 0.066 | 0.070 | 0.068 |
| 0.1 | 0.110 | 0.129 | 0.019 | 0.129 | 0.019 | 0.125 | 0.015 |
| | 0.125 | 0.130 | 0.005 | 0.120 | -0.005 | 0.130 | 0.005 |
| 1 | 0.245 | 0.255 | 0.010 | 0.220 | -0.025 | 0.212 | -0.033 |
| | 0.229 | 0.233 | 0.004 | 0.216 | -0.013 | 0.209 | -0.020 |
| 10 | 0.377 | 0.379 | 0.002 | 0.360 | -0.017 | 0.355 | -0.022 |
| | 0.373 | 0.374 | 0.001 | 0.367 | -0.006 | 0.362 | -0.011 |
| 100 | 0.490 | 0.491 | 0.001 | 0.470 | -0.020 | 0.472 | -0.018 |
| | 0.496 | 0.501 | 0.005 | 0.475 | -0.021 | 0.477 | -0.022 |

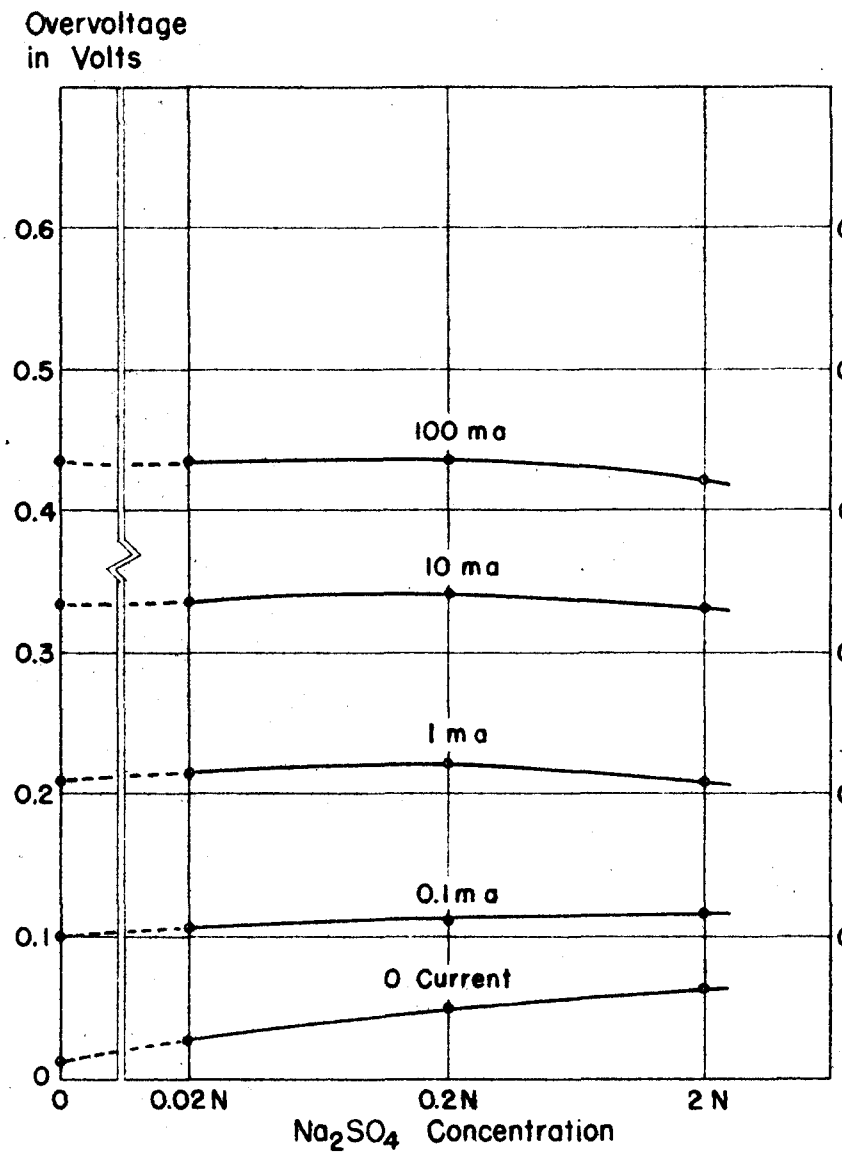


Fig. 17 $Na_2SO_4$ Added to 0.2 N NaOH

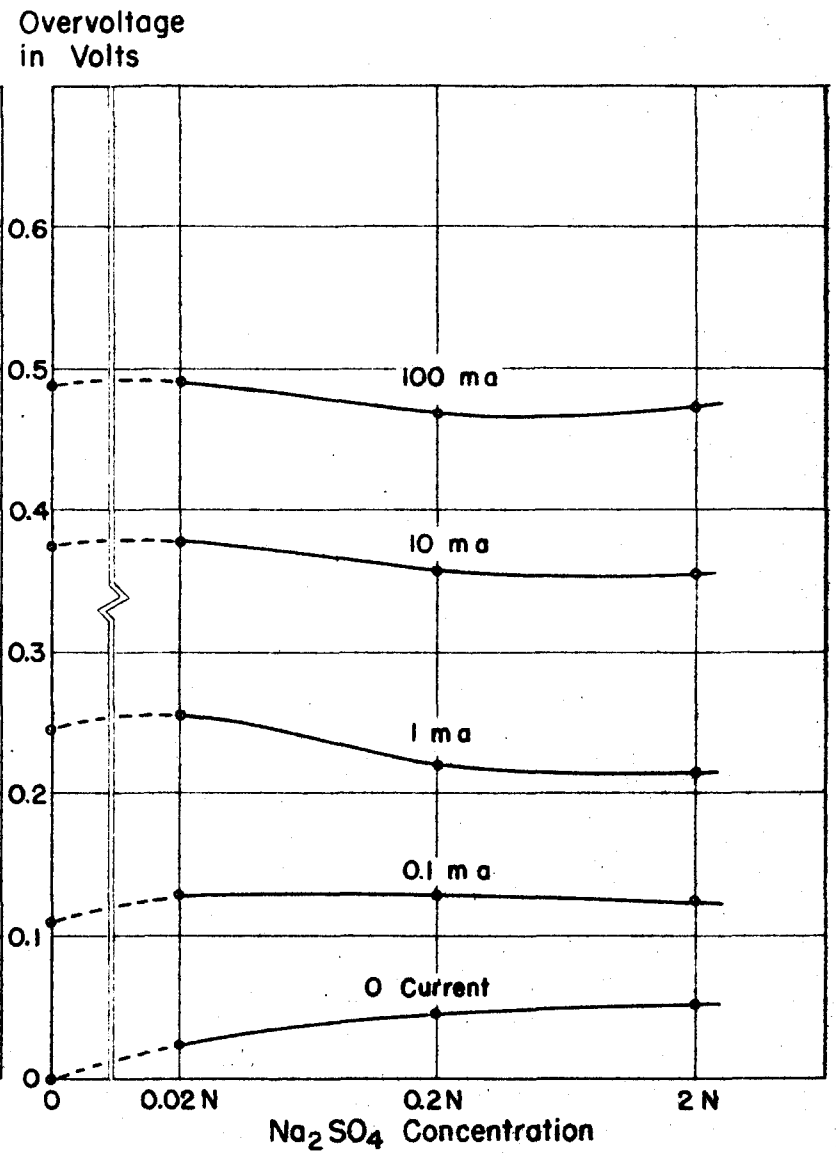


Fig. 18 $Na_2SO_4$ Added to 0.02 N NaOH

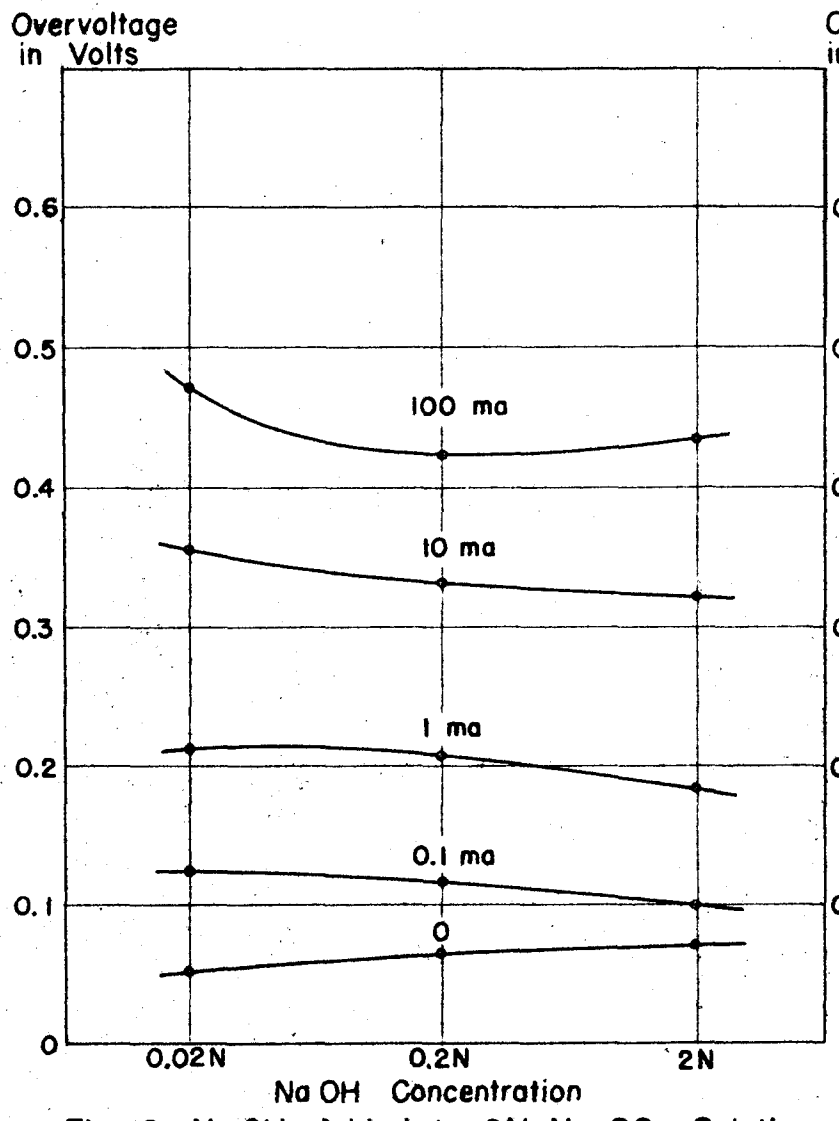


Fig. 19 Na OH Added to 2N $Na_2SO_4$ Solution

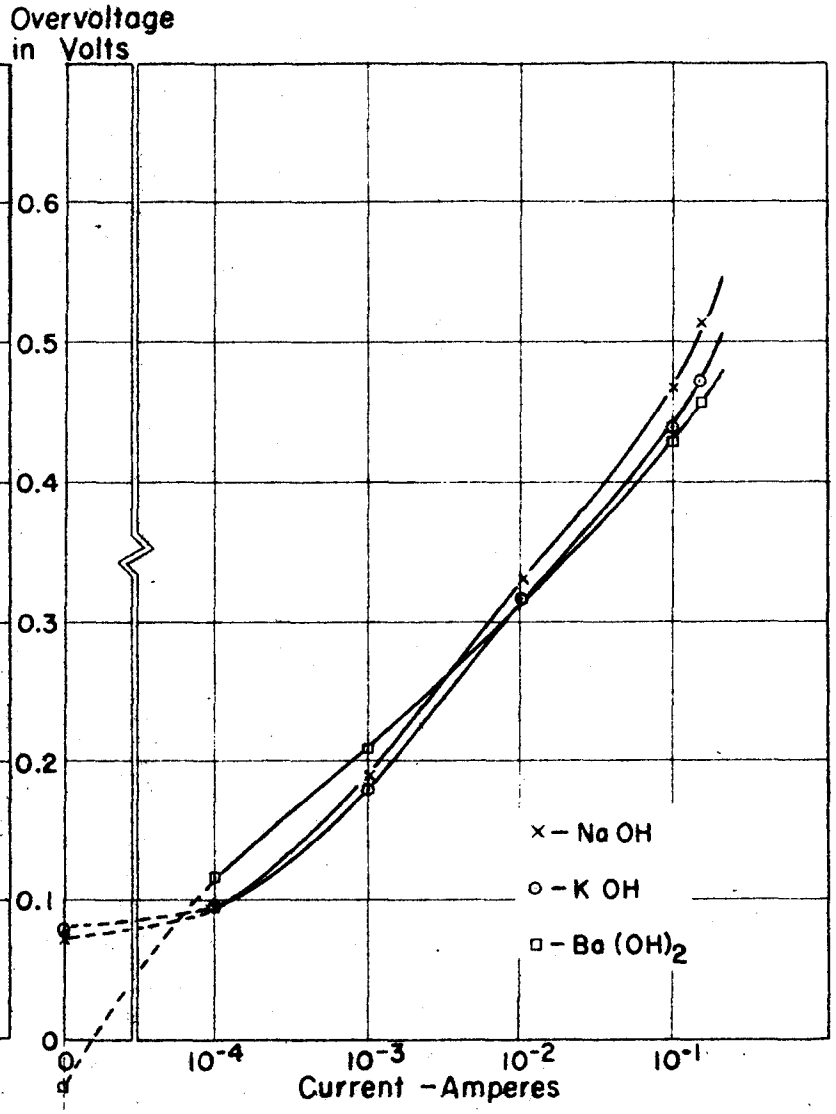


Fig. 20 Current-Overvoltage Curves for Different Bases

Effect of cations on overvoltage.

Table 13 condenses the data on 2N solutions of NaOH and KOH and on a 0.5N solution of $Ba(OH)_2$. Curves plotted from Table 13 are shown in Figure 20. These show that NaOH has consistently higher overvoltage values than KOH; furthermore, the difference increases with increasing current density. On the other hand, $Ba(OH)_2$ has higher values at the low densities and lower values at the high densities than either NaOH or KOH.

Table 13

Current-Overvoltage Data for Different Bases

| Current (ma) | 2N-NaOH $\eta$ (in volt) | 2N-KOH $\eta$ (in volt) | 0.5N-$Ba(OH)_2$ $\eta$ (in volt) |
|---|---|---|---|
| 0 | 0.071 | 0.080 | -0.034 |
| 0.1 | 0.096 | 0.094 | +0.117 |
| 1 | 0.188 | 0.180 | 0.209 |
| 10 | 0.325 | 0.317 | 0.315 |
| 100 | 0.466 | 0.439 | 0.429 |
| 150 | 0.512 | 0.471 | 0.459 |

In Table 14 are gathered the data from 2N solutions of the chlorides in 0.2N solutions of the respective hydroxides of sodium, potassium, and barium. The curves in Figure 21 present the same material graphically. Again it may be seen that overvoltage values for the potassium solutions are consistently lower than the corresponding sodium values. But in this figure the values for the barium solution are now

higher than either of the others for the course of the curves except at no current.

Table 14

Effect of Cations on Overvoltage

| Current (ma) | 2N-NaCl +0.2N-NaOH $\eta$ (v) | 2N-KCl +0.2N-KOH $\eta$ (v) | 2N-$BaCl_2$ +0.2N-$Ba(OH)_2$ $\eta$ (v) |
|---|---|---|---|
| 0 | 0.056 | 0.060 | -0.077 |
| 0.1 | 0.086 | 0.085 | +0.086 |
| 1 | 0.193 | 0.176 | 0.208 |
| 10 | 0.328 | 0.295 | 0.326 |
| 100 | 0.431 | 0.387 | 0.439 |
| 150 | 0.459 | 0.409 | 0.470 |

Effect of anions on overvoltage.

Table 15 and Figure 22 show the material gathered from measurements on 2N-NaOH solutions containing various salts. The measurements were all made according to Procedure A but were not carried out in one series so may not be comparable. The $Na_2SiO_3$-curve has a rather surprising course which is echoed to some degree in the $NaAlO_2$-curve. The upswing in all the curves at the end probably is due to a greater actual increase in current density than the numbers indicate; that is, the surface of the electrode available for discharging purposes is probably less than at lower densities.

Table 15

Effect of Anions on Overvoltage
(Salts added to 2N-NaOH Solutions)

| Current (ma) | Sat'd $Na_3PO_4$ $\eta$ (v) | 0.7N-$NaAlO_2$ + 2N-$Na_2SO_4$ $\eta$ (v) | 2N-$Na_2SiO_3$ $\eta$ (v) | 2N-NaCl $\eta$ (v) | No salt added $\eta$ (v) |
|---|---|---|---|---|---|
| 0 | 0.104 | 0.098 | 0.086 | 0.089 | 0.095 |
| 0.1 | 0.285 | 0.162 | 0.125 | 0.279 | 0.207 |
| 1 | 0.404 | 0.282 | 0.298 | 0.394 | 0.336 |
| 10 | 0.515 | 0.411 | 0.388 | 0.494 | 0.460 |
| 100 | 0.580 | 0.490 | 0.437 | 0.590 | 0.573 |
| 150 | 0.615 | 0.517 | 0.454 | 0.612 | 0.615 |

Incidental observations.

Occasionally in the course of a run, particularly one carried out according to Procedure A, the electrode would assume an "elevation" state. That is, the overvoltage would amount to two volts or more at a current of ten milliamperes but would decrease with decreasing currents to either the same value as ordinarily or less. Transitions in either direction to or from the "elevation" state proceeded practically instantaneously. The conditions required to obtain this state seemed to be small concentrations, high polarizations, and better than ordinary exclusion of the anode liquid.

It was observed also that large concentrations seemed to "stabilize" the value of the overvoltage at no current. That is, this value would be quickly reached on the descending set of readings and would hold quite constantly for

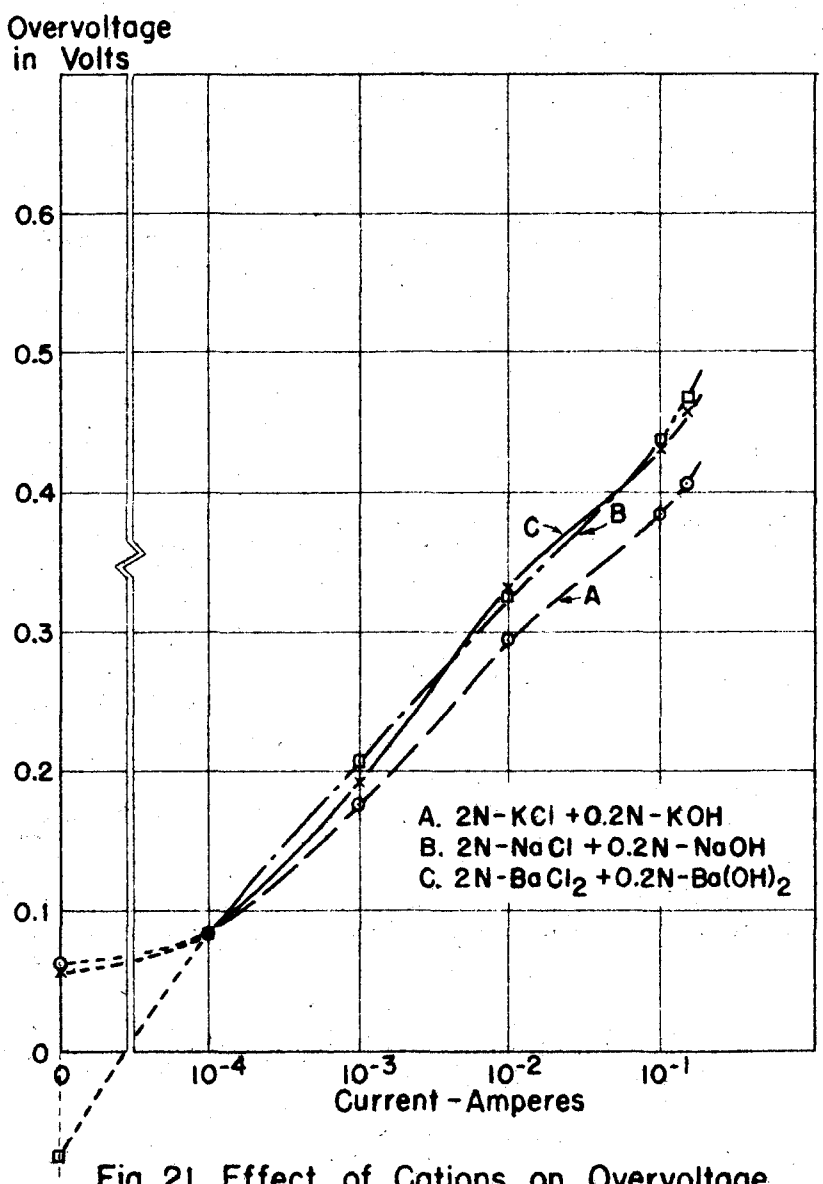


Fig. 21 Effect of Cations on Overvoltage

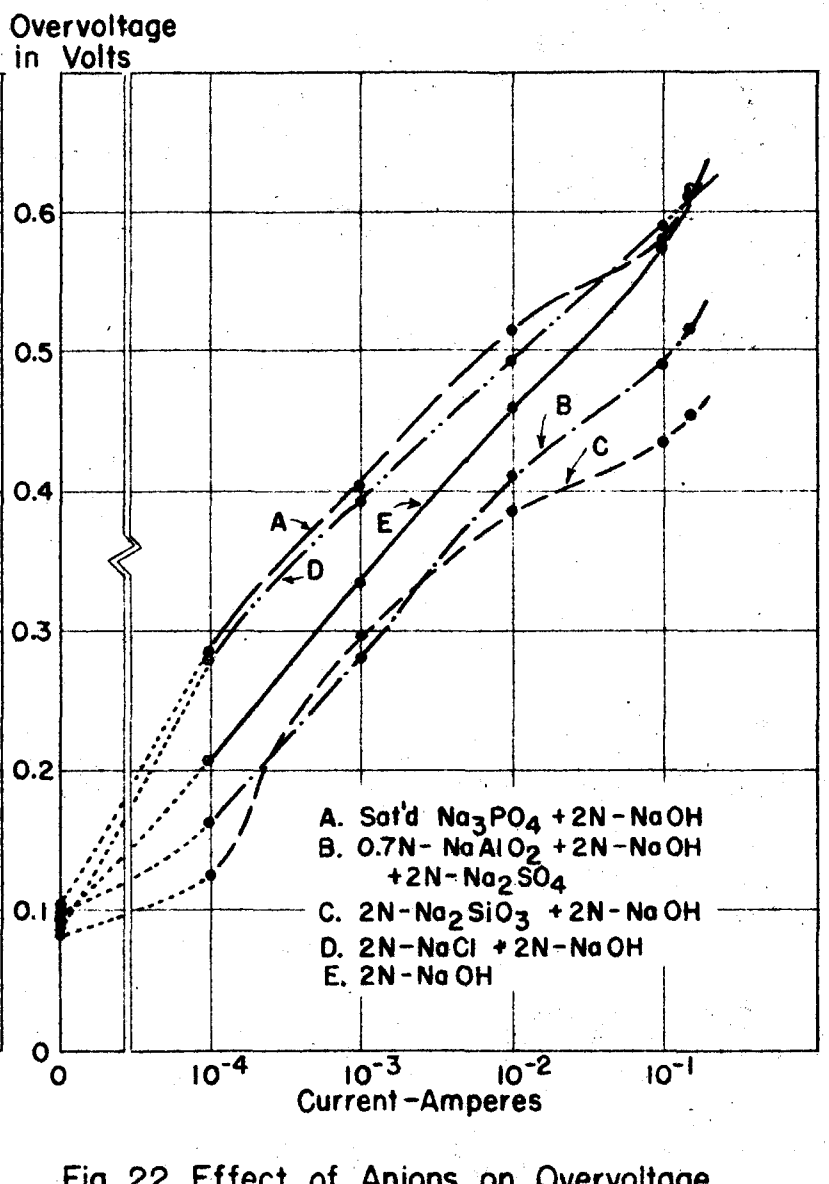


Fig. 22 Effect of Anions on Overvoltage

considerable time; on the other hand, in small concentrations the overvoltage continually dropped and in a relatively short period possessed negative values.

Similarly check values for current strengths of one and ten millamperes were more closely related and more easily obtained than at any of the other current strengths.

Interpretation of results relative to corrosion.

Many of the results observed in the foregoing may be explained if the assumption is made that the point of zero surface charge on an iron electrode lies in the neighborhood of 1.35 volts relative to the saturated calomel electrode. This corresponds closely to overvoltages of 0.3-0.4 volt in the region at which these experiments were prosecuted.

At lower overvoltages, the $\zeta$ -potential* is positive and at higher overvoltages negative. Hence, at the low polarizations the $\zeta$ -potential is affected by the negatively charged ions and vice versa at the higher polarizations. Since $\zeta$ is a function of $\varphi$ (the electrode potential) in the neighborhood of zero surface charge, the equation of Lukovtsev, Levina, and Frumkin,

$$\eta = -\zeta + 2RT/F \ln i - RT/F \ln C_{OH^-} ,$$

must be applied with due consideration. Moreover, the

*The $\zeta$ -potential used here and elsewhere in this paper is not necessarily the same as the $\zeta$ -potential used in electrokinetics but is closely allied to it.

surface charge (and the $\zeta$ -potential) will vary with changing hydroxide-ion concentration in this region, particularly at the low concentrations where the surface is the least saturated.

Inspection of Figures 16 and 19 shows that $\zeta$ is relatively more affected in the low concentrations at the high polarizations. This effect seems to be the most marked at a potential of 1.35 volts. Similarly, Figures 17 and 18 seem to show that the effect of the sulfate ion in lowering (making it less positive) is also a maximum at this potential.

In Figure 20, the barium ion appears to become operative at about the above potential. That is, the normally negative charge is neutralized by the barium ion causing a less negative $\zeta$ -potential and, therefore, a smaller $\eta$.

Therefore, since the reversible hydrogen potential in neutral solutions is about 0.650 volt, the $\zeta$ -potential at an iron surface must be positive; hence, it is subject to the effect of negative ions. The results of Herasymenko and Šlendyk showed that minute concentrations of $LaCl_3$ raised the overvoltage on mercury where a negative $\zeta$ -potential is existent. Analogously, small amounts of $Na_3PO_4$ should increase the overvoltage at an iron surface where a positive $\zeta$ -potential occurs.

## SUMMARY

1. A literature search revealed that the overvoltage developed at an electrode surface is dependent on the composition of the solution.

2. A theoretical explanation for the effect on overvoltages at mercury and nickel electrodes is present in the literature.

3. The experimental procedure was discussed.

4. The effect of changing NaOH concentration was observed to be greatest at low concentrations, the more so the higher the electrode potential. This effect was observed both in simple NaOH solutions and in those containing $Na_2SO_4$.

5. The overvoltage was observed to increase at low densities, pass through a maximum at medium densities, and decrease at high densities with increasing $Na_2SO_4$ concentrations in solutions of constant NaOH concentration. The maximum was observed to occur at the point where the $Na_2SO_4$ concentration equalled the NaOH concentration.

6. The $\eta$ -log i curve for $Ba(OH)_2$ solution was observed to bend downward on increasing polarizations.

7. A possible explanation for the inhibiting action of phosphate ion on corrosion of iron was presented.

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